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Volume 3

1950

	Pages		*Pages*
CLASSIFIED CONTENTS	*v*	MAY	197–244
AUTHOR INDEX	*viii*	JUNE	245–292
NAME INDEX	*xii*	JULY	293–340
CORRECTIONS	*xxviii*	AUGUST	341–388
JANUARY	1–52	SEPTEMBER	389–436
FEBRUARY	53–100	OCTOBER	437–484
MARCH	101–148	NOVEMBER	485–532
APRIL	149–196	DECEMBER	533–584

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Classified Contents

Chairman's Note 533

COMMENTARIES

Research and Practice in Industrial Relations *E Wight Bakke* 1
Higher Education for Technologists *A R Ubbelohde* 53
Science—its Sphere of Influence *E C Stakman* 101
Scientific Research in Industry *P Chevenard* 149
Mathematics in the Larger Context *H W Turnbull* 197
Progress in Manual and Automatic Control Apparatus *A Tustin* 245
An Evaluation of Animal and Human Mentality *M Burton* 293
Japanese Science and Technology *H C Kelly* 341
Pleasure and Pursuit in Science *K G Denbigh* 389
Specialized Scientific Training and Citizenship *K Lonsdale* 437
Scientific Views of Man *J A V Butler* 485

REVIEW ARTICLES

Absorption, Gas *D W van Krevelen* 106
Absorption of Sound by Porous Materials *C Zwikker* 400
Acoustic Waves, Powerful *P Alexander* 68
Activation Processes in the Sensitiveness of Explosives *A R Ubbelohde* 207
Air, Measurements in the Upper, by Radio Sonde *E G Dymond* 345
Amalgam Metallurgy, Applications of *H Hohn* 407
Amines, Reaction between Nitrous Acid and *J C Earl* 120
Analysis of Complex Organic Compounds, X-Ray Structure *J D Dunitz* 6
Analysis of Silicates, Rapid *J Gillis* 74
Application, Development and, of High Vacuum Technique *M Pirani* 540
Applications of Amalgam Metallurgy *H Hohn* 407
Applications of the Electronic Theory of Organic Reactions *M J S Dewar* 154
Applications, Some, of Servomechanisms *A Porter* 166
Artificial Lactation and Perfusion of the Bovine Mammary Gland *G Peeters and L Massart* 217
Atomization of Carbon, Heat of *H D Springall* 260

Beetle, Colorado, Problem *C T Gimingham* 310
Breeding Research, Livestock *I L Mason* 171

Carbon, Heat of Atomization of *H D Springall* 260
Carotenoids and Vitamin A *R F Hunter* 453
Centimetre Wavelengths, Spectroscopy at *B Bleaney* 490
Chemical Metallurgy, Mercury in *H Hohn* 16
Chemistry of Lignin *H Erdtman* 63
Chemistry of Specific, Selective and Sensitive Reactions *F Feigl* 550
Chemoreceptors and Regulation of Respiration *C Heymans* 355
Chromatography, Ion Exchange Resins in *C W Davies* 447
Cocoa Production, Research and *E E Cheesman* 12
Colorado Beetle Problem *C T Gimingham* 310
Complex Organic Compounds, X-Ray Structure Analysis of *J D Dunitz* 6
Conduction Electrons in Non-metallic Solids *H Frohlich* 202
Crystals, Study of Imperfect, by Powder Photographs *A J C Wilson* 394
*Cyclo*hexane Stereochemistry of *O Hassel* 504
Cytochemistry, Micromethods in Histochemistry and *H Holter and K Linderstrom-Lang* 315

Design, Experimental *M H Quenouille* 213
Development and Application of High Vacuum Technique *M Pirani* 540

Electrical Properties of Muscle Fibre *B Katz* 359
Electronic Theory of Organic Reactions, Applications of the *M J S Dewar* 154
Electrons, Conduction, in Non-metallic Solids *H Frohlich* 202
Erosion, Water *W A T Summerville* 547
Estimation of Vitamins A, Recent Advances in *V H Booth* 497
Experimental Design *M H Quenouille* 213
Explosives, Activation Processes in the Sensitiveness of *A R Ubbelohde* 207

Filtration, Industrial *P M Heertjes* 254
Fluidization of Masses of Particles *R H Wilhelm* 159
Fluorine and Teeth *J M Fletcher and R H S Robertson* 23
Fringe Orders, Measuring, in Photoelasticity *W A P Fisher* 298

Gas Absorption *D W van Krevelen* 106
Gland, Artificial Lactation and Perfusion of the Bovine Mammary *G Peeters and L Massart* 217
Grafting *R J Garner* 248
Gram Staining Reaction for Micro-organisms *M Webb* 113

Heat of Atomization of Carbon *H D Springall* 260
High Vacuum Technique, Development and Application of *M Pirani* 540
Histochemistry and Cytochemistry, Micromethods in *H Holter and K Linderström-Lang* 315
Honey and its Botanical Sources *F N Howes* 127

Industrial Filtration *P M Heertjes* 254
Ion Exchange Resins in Chromatography *C W Davies* 447

Knowledge of Wool Structure, Recent Advances in *H Lindley* 509

Lactation, Artificial, and Perfusion of the Bovine Mammary Gland *G Peeters and L Massart* 217
Lignin, Chemistry of *H Erdtman* 63
Livestock Breeding Research *I L Mason* 171

Manurial Problems of Marginal Land *W Ellison* 58
Masses of Particles, Fluidization of *R H Wilhelm* 159
Measurements in the Upper Air by Radio Sonde *E G Dymond* 345
Measuring Fringe Orders in Photoelasticity *W A P Fisher* 298
Mercury in Chemical Metallurgy *H Hohn* 16
Metallurgy, Amalgam, Applications of *H Hohn* 407

Micromethods in Histochemistry and Cytochemistry *H Holter and K Linderström-Lang* 315
Micro-organisms, Gram Staining Reaction for *M Webb* 113
Muscle Fibre, Electrical Properties of *B Katz* 359

Nitrous Acid and Amines, Reaction between *J C Earl* 120
Non-metallic Solids, Conduction Electrons in *H Fröhlich* 202

Organic Reactions, Applications of the Electronic Theory of *M J S Dewar* 154
Orthoesters of Silicon, Titanium and Zirconium *W Wardlaw and D C Bradley* 462

Particles, Fluidisation of Masses of *R H Wilhelm* 159
Perfusion of the Bovine Mammary Gland, Artificial Lactation and *G Peeters and L Massart* 217
Photocopying Processes for the Research Worker *B de Gorter* 417
Photoelasticity, Measuring Fringe Orders in *W A P Fisher* 298
Porous Materials, Absorption of Sound by *C Zwikker* 400
Powder Photographs, Study of Imperfect Crystals by *A J C Wilson* 394
Powerful Acoustic Waves *P Alexander* 68
Processes, Activation, in the Sensitiveness of Explosives *A R Ubbelohde* 207
Processes, Photocopying, for the Research Worker *B de Gorter* 417
Progress, Recent, in Refractories *J H Chesters* 303
Properties, Electrical, of Muscle Fibre *B Katz* 359
Psychophysical Relationships and their Study *R Harper* 350

Radio Sonde, Measurements in the Upper Air by *E G Dymond* 345
Rapid Analysis of Silicates *J Gillis* 74
Reaction between Nitrous Acid and Amines *J C Earl* 120
Reaction for Micro-organisms, Gram Staining *M Webb* 113
Reactions, Applications of the Electronic Theory of Organic *M J S Dewar* 154
Recent Advances in Estimation of Vitamins A *V H Booth* 497
Recent Advances in Knowledge of Wool Structure *H Lindley* 509
Refractories, Recent Progress in *J H Chesters* 303
Regulation of Respiration, Chemoreceptors and *C Heymans* 355
Relationships, Psychophysical, and their Study *R Harper* 350
Research and Cocoa Production *E E Cheesman* 12
Research, Livestock Breeding *I L Mason* 171
Resins, Ion Exchange, in Chromatography *C W Davies* 447
Respiration, Chemoreceptors and Regulation of *C Heymans* 355

Sensitiveness of Explosives, Activation Processes in the *A R Ubbelohde* 207
Servomechanisms, Some Applications of *A Porter* 166
Silicates, Rapid Analysis of *J Gillis* 74
Silicon, Orthoesters of, Titanium and Zirconium *W Wardlaw and D C Bradley* 462
Some Applications of Servomechanisms *A Porter* 166
Sound, Absorption of, by Porous Materials *C Zwikker* 400
Sound Writing and Reading *C J Overbeck* 268
Sources, Honey and its Botanical *F N Howes* 127
Specific, Selective and Sensitive Reactions, Chemistry of *F Feigl* 550
Spectroscopy at Centimetre Wavelengths *B Bleaney* 490
Stereochemistry of Cyclohexane *O Hassel* 504
Structure Analysis, X-Ray, of Complex Organic Compounds *J D Dunitz* 6
Study of Imperfect Crystals by Powder Photographs *A J C Wilson* 394
Study, Psychophysical Relationships and their *R Harper* 350
Superconductivity *Aaron Wexler* 534

Teeth, Fluorine and *J M Fletcher and R H S Robertson* 23
Theory of Organic Reactions, Applications of the Electronic *M J S Dewar* 154
Titanium, Orthoesters of Silicon, and Zirconium *W Wardlaw and D C Bradley* 462

Ultracentrifuge, The *H Gutfreund* 442

Vitamin A, Carotenoids and *R F Hunter* 453
Vitamins A, Recent Advances in Estimation of *V H. Booth* 497

Water Erosion *W A T Summerville* 547
Wool Structure, Recent Advances in Knowledge of *H. Lindley* 509

X-Ray Structure Analysis of Complex Organic Compounds *J D Dunitz* 6

Zirconium, Orthoesters of Silicon, Titanium and *W Wardlaw and D C Bradley* 462

RESEARCH ESTABLISHMENTS

Armour Research Foundation of Illinois Institute of Technology *H A Leedy* 27
Baking Industries Research Station Measuring the Physical Characteristics of Bread *S J Cornford and J B M Coppock* 558
Cawthron Institute, New Zealand *Sir Theodore Rigg* 131
Forest Research Institute of Sweden *M Näslund* 320
Institut d'Optique Théorique et Appliquée, Paris *P Fleury and A Maréchal* 176
Irrigation Requirements in Spain *L Cavanillas* 365
Laboratories of the Carlsberg Foundation *H Holter* 274
Permanent Magnet Association Central Research Laboratory *K Hoselitz* 77
Road Research Laboratory of the D S I R *W H. Glanville* 514

Rowett Research Institute *D P Cuthbertson* 222
The Merck Research Laboratories *C R Addinall* 420
The Printing, Packaging and Allied Trades Research Association *G L Riddell* 465

FORUM

MATHEWS, S Interfacial Tension of Medicinal Paraffin/Water 225
TAYLOR, G I Defence Services Research Facilities 34
ZUCKER, F J Mathematics in the Larger Context 326

BOOK REVIEWS

BENNETT, G M on *Recent Advances in Analytical Chemistry*, edited by R E Burk and O Grummitt 519
BRETSCHER, E on G Devons *Excited States of Nuclei* 568
BURTON, M on H Hediger *Wild Animals in Captivity* 471
BUTLER, J A V on M Calvin, C Heidelberger, J C Reid, B M Tolbert and P F Yankwich *Isotopic Carbon, Techniques in its Measurement and Chemical Manipulation* 229

CALLAN, H G on C D Darlington and K Mather *The Elements of Genetics* 565
CAMPBELL, W G on E Glesinger *The Coming Age of Wood* 375
CHALMERS, B on A H Sully *Metallic Creep and Creep Resistant Alloys* 32
COSSLETT, V F on R W G Wyckoff *Electron Microscopy Technique and Applications* 565
CRAGGS, J D on V K Zworykin and E G Ramberg *Photoelectricity and its Application* 138
CRUMP, L M on J Duché *La Biologie des Sols* 373

DARLINGTON, C D on E D P de Robertis, W W Nowinski and F A Saez (translated by W Andrew) *General Cytology* 229
DIAMOND, C on B L Davies *Technology of Plastics* 372
DUNWORTH, J V on B B Rossi and H H Staub *Ionization Chambers and Counters Experimental Techniques* 564
— on S C Curran and J D Craggs *Counting Tubes Theory and Applications* 564

EMELÉUS, H J on *Gmelin's Handbuch der Anorganischen Chemie*, 8th edition, edited by E H E Pietsch *No 18 Antimony, Parts B2, B3 No 68 Platinum, Part A5* 32
— *ibid No 35 Aluminium, Part A8* 426
— *ibid No 10 Selenium, Part A2 No 28 Calcium, Part A1, No 62 Gold, Part A1* 472
— on G Hagg (translated into German by H Baumann from 4th Swedish edition) *Die theoretischen Grundlagen der analytischen Chemie* 328

FINNEY, D J on M H Quenouille *Introductory Statistics* 563
FISHER, W A P on A W Hendry *An Introduction to Photo-elastic Analysis* 328
— on M M Frocht *Photoelasticity, Vol II* 284
FRANZINETTI, C on E Perucca *Trattato di Fisica Generale e Sperimentale*, 6th Italian edition 85

GARNER, F H on *Encyclopedia of Chemical Technology, Vol II*, edited by R E Kirk and D F Othmer 329
GARNER, W E on J R Partington *Advanced Treatise on Physical Chemistry, I Fundamental Principles, Properties of Gases* 137
GARTON, C G on E May *Industrial High Frequency Electric Power* 372
— on L Hartshorn *Radio-Frequency Heating* 372
GAYDON, A G on R C Johnson *An Introduction to Molecular Spectra* 375
GILBERT, C L on R F Goldstein *The Petroleum Chemicals Industry* 425
GLUECKAUF, E on *Frontiers in Chemistry, Vol VIII Frontiers in Colloid Chemistry*, edited by R E Burk and O Grummitt 283
GODDARD, L S on *M I T Series Vol XIX Waveforms*, edited by C Chance F C Williams, V Hughes, E F MacNichol and D Sayre 85
— on C Cherry *Pulses and Transients in Communication Circuits* 85
— on W O Schumann *Elektrische Wellen* 85
GOLDIE, A H R on M V Wilkes *Oscillations of the Earth's Atmosphere* 139
— on O G Sutton *Atmospheric Turbulence* 139
GOODWIN, E T on R Taton *Le Calcul Mécanique* 138
GOUDSMIT, S A on M L Oliphant, P M S Blackett, R F Harrod, B Russell, L Curtis and D W Brogan *The Atomic Age Sir Halley Stewart Lectures for 1948* 184

HARDWICK, P J on *Analytica Chimica Acta Special Supplement Analytical Chemistry and Chemical Analysis, 1948* 374
HARLAND, S C on G R Harrison *Atoms in Action* 373
HALSALL, T G on F J Smith and E Jones *A Scheme of Qualitative Organic Analysis* 183
HANNAH, M on A Brearley and D R Cox *An Outline of Statistical Methods for Use in the Textile Industry* 285
— on W I R A publication *Wool Research 1918–1948, Vol 4 Carding, Vol 6 Drawing and Spinning* 285
HUGHES, A on W Kuhl *Die technischen Grundlagen der kinematischen Zellforschung* 567

INGOLD, C T on E J H Corner *A Monograph of Clavaria and Allied Genera* 426

KOLB, O K on C Zwikker and C W Kosten *Sound Absorbing Materials* 282
KUHN, W on L R G Treloar *The Physics of Rubber Elasticity* 138

LAMPITT, L H on J B S Braverman *Citrus Products. Chemical Composition and Chemical Technology* 34
LANDSBERG, P T on W Heisenberg *Two Lectures* 567

MADDOCK, A G on G Friedlander and J W Kennedy *Introduction to Radiochemistry* 473
MEARA, L on A W Ralston *Fatty Acids and their Derivatives* 330
MEGSON, N J L on *Monomers, I*, edited by E R Blout, W P Hohenstein and H Mark 374
MILLAR, A R on M Born and H S Green *A General Kinetic Theory of Liquids* 471
MOORE, H on J M Stevels *Progress in the Theory of the Physical Properties of Glass* 283

PARTINGTON, J R on M J S Dewar *Electronic Theory of Organic Chemistry* 182

Reiner, M on G. W Scott Blair *A Survey of General and Applied Rheology*, 2nd edition 228
Robinson, A on R Courant and K O Friedrichs *Supersonic Flow and Shock Waves* 373
Roughton, F J W on R Lemberg and J W Legge *Hematin Compounds and Bile Pigments their Constitution, Metabolism, and Function* 329

Sayers, J on C H Bachman *Techniques in Experimental Electronics* 371
— on D Taylor and C H Westcott *Principles of Radar* 284
Schulman, J H on A M Schwartz and J W Perry *Surface Active Agents Their Chemistry and Technology* 566
Shoppee, C W on *Technique of Organic Chemistry, Vol II C[illegible]lytic, Photochemical and Electrolytic Reactions*, edited by A Weissberger 472
Sondheimer, E H on E Justi *Leitfähigkeit und Leitungsmechanismus fester Stoffe* 139
Vick, F A on H K Henisch *Metal Rectifiers* 519
Vogel, A I on F D and C F Snell *Colorimetric Methods of Analysis*, 3rd edition, Vol I *Theory, Instruments, pH* 183

Waddington, C H on K Mather *Biometrical Genetics, The Study of Continuous Variation* 228
Waldram, J M on B F Fedorov, translated by W. R Stoker *Lighting Technique* 33
Webb, M on E G Clayden *Practical Section Cutting and Staining* 184
Wright, W D on P J Bouma (English edition) *Physical Aspects of Colour* 285
— on M H Pirenne *Vision and the Eye* 564

Youd, C S on A C Clarke *Interplanetary Flight* 330
Young, J Z on L von Bertalanffy *Das biologische Weltbild, I die Stellung des Lebens in Natur und Wissenschaft* 282

MISCELLANEOUS NOTES
These begin on pages 31, 82, 135, 180, 226, 279, 326, 370, 424, 470, 518, 562

BOOKS TO COME
These begin on pages 34, 85, 139, 184, 229, 285, 330, 375, 426, 473

RESEARCH SUPPLEMENT
For papers and correspondence in the Research Supplement, reference should be made to the Author Index, which follows, where the titles of such papers and correspondence are shown in italic type

Author Index

Addinall, C R The Merck Research Laboratories 420
Alexander, P Powerful Acoustic Waves 68
Allen, J E *Voltage Gradients in High Current Spark Channels* 527
Amble, E (and O Hassel) *Dipole Moment of 1,2,3,4,5,6-Hexachlorocyclohexane* 52
Anderson, Sir John Chairman's Note 533
Archard, J F (and P L Clegg and A M Taylor) *Photoelectric Methods for Metal Optics* 339

Bakke, E Wight Research and Practice in Industrial Relations 1
Banks, W H (and R R Coupe) *Adsorption of Cobalt Naphthenate by Cellulose Fibres* 528
Barker, A N (and H O W Richardson and N Feather) *An Emission Microscope for Photoelectron Radiography* 431
Bauer, L (and J Cymerman) *Ultraviolet Absorption Spectra of Some Aromatic Disulphides and Disulphoxides* 146
Berry, R L (and M B Waldron and G V Raynor) *Outer Brillouin Zones for the Face-centred Cubic, Body-centred Cubic and Close Packed Hexagonal Structures* 195
Bleaney, B Spectroscopy at Centimetre Wavelengths 490
Booth, V H Recent Advances in Estimation of Vitamin A 497
Bowden, F P *Frictional Properties of Porous Metal Impregnated with Plastic* 147
— *Frictional Properties of Porous Metals Containing Molybdenum Disulphide* 383
— (and L Young) *Influence of Interfacial Potential on Friction and Surface Damage* 235
Bowden, F P (and K V Shooter) *Frictional Behaviour of Plastics Impregnated with Molybdenum Disulphide* 384
Bowen, K W J (and T P Hoar) *Low Temperature Ferromagnetism of Sigma Phase in an Alloy Steel* 484
Bradley, D C (and W Wardlaw) Orthoesters of Silicon, Titanium and Zirconium 462
Braun, I (and H Frey and M Reiner) *Mechanism of the Weissenberg Effect* 243
Bretscher, E Book review 568
Bright, N F H (and T Carson and T A Dyson) *Azobenzene Part I Vapour Pressure of Cis- and Trans-azobenzene* 185
Brown, M J (and A G Foster) *Effect of Molecular Size on Sorption Hysteresis* 97
Burton, M An Evaluation of Animal and Human Mentality 293
— Book review 471
Butler, J A V Book review 229
— Scientific Views of Man 485

Calderwood, J H (and R Cooper and H K Heppel) *The Dielectric Properties of Copper Oxide Rectifiers* 530
Callan, H G Book review 565
Campbell, W G Book review 375
Carson, T (and N F H Bright and T A Dyson) *Azobenzene Part I Vapour Pressure of Cis- and Trans-azobenzene* 185
Cavanillas, L Irrigation Requirements in Spain 365
Chalmers, B Book review 32
Cheesman, E E Research and Cocoa Production 12
Chesters, J H Recent Progress in Refractories 303

Chevenard, P Scientific Research in Industry 149
Clegg, P L (and J F Archard and A M Taylor) *Photoelectric Methods for Metal Optics* 339
Cooper, R (and J H Calderwood and H K Heppel) *The Dielectric Properties of Copper Oxide Rectifiers* 530
Coppock, J B M (and S J Cornford) Baking Industries Research Station Measuring the Physical Characteristics of Bread 558
Cornford, S J (and J B M Coppock) Baking Industries Research Station Measuring the Physical Characteristics of Bread 558
Cosslett, V E Book review 566
Coupe, R R (and W H Banks) *Adsorption of Cobalt Naphthenate by Cellulose Fibres* 528
Courtney-Pratt, J S *A Cleavage Step on Mica with a Height that is a Half-integral Multiple of the Crystal Lattice Spacing* 47
Craggs, J D Book review 137
Crook, A W (and W Hirst) *Adhesion of Indium under Static and Dynamic Loading* 432
Crump, L M Book review 373
Cuthbertson, D P Rowett Research Institute 222
Cymerman, J (and L Bauer) *Ultraviolet Absorption Spectra of Some Aromatic Disulphides and Disulphoxides* 146

Darlington, C D Book review 228
Davies, C W Ion Exchange Resins in Chromatography 447
Day, L A (and E R Ward) *Relation between Structure and Melting Point in Aromatic Compounds* 580
Debot, R *Measurements on Enlargements on Plates and the Construction of a New Type of Photoelectric Granularity Meter* 91
— *Variation of Granularity of a Photographic Deposit with Area of Scanning Spot* 474
de Gorter, B Photocopying Processes for the Research Worker 417
de la Mare, P B D (and E D Hughes and C A Vernon) *Mechanism of Aromatic Halogenation, The Chlorine Cation,* Cl^+ 192
Denbigh, K G Pleasure and Pursuit in Science 389
— (and G Raumann and I S Nixon) *Reaction of Chlorine Cations with Olefins* 242
— — — *Transition between Laminar and Turbulent Flow in Various Liquids* 520
Dewar, M J S Applications of the Electronic Theory of Organic Reactions 154
Diamond, C Book review 372
Drake, C F *The Chemical Silvering of Non-metallic Surfaces* 582
Dunitz, J D X-Ray Structure Analysis of Complex Organic Compounds 6
Dunworth, J V Book review 565
Dymond, E G Measurements in the Upper Air by Radio Sonde 345
Dyson, T A (and N F H Bright and T Carson) *Azobenzene Part I. Vapour Pressure of Cis- and Trans-azobenzene* 185

Earl, J C Reaction between Nitrous Acid and Amines 120
Ellison, W Manurial Problems of Marginal Land 58
Emeléus, H J Book reviews 32, 327, 426, 472
Erdtman, H Chemistry of Lignin 63
Evans, W M (and A R Ubbelohde) *Formation of Munroe Jets and their Action on Massive Targets* 331
— (and A R Ubbelohde) *Some Kinematic Properties of Munroe Jets* 376

Feather, N (and A N Barker and H O W Richardson) *An Emission Microscope for Photoelectron Radiography* 431
Feigl, F Chemistry of Specific, Selective and Sensitive Reactions 550
Finney, D J Book review 564
Fisher, W A P Book reviews 283, 328
— Measuring Fringe Orders in Photoelasticity 298
Fletcher, J M (and R H S Robertson) Fluorine and Teeth 23
Fleury, P (and A Maréchal) Institut d'Optique Théorique et Appliquée, Paris 176
Foster, A G (and M J Brown) *Effect of Molecular Size on Sorption Hysteresis* 97
Franzinetti, C Book review 85
Frey, H (and I Braun and M Reiner) *Mechanism of the Weissenberg Effect* 243
Frohlich, H Conduction Electrons in Non-metallic Solids 202

Gadsby, G N *Synthesis of Organo-silicon Carboxylic Acids* 338
Garner, F H Book review 328
Garner, R J Grafting 248
Garner, W E Book review 136
Garton, C G Book review 371
Gaydon, A G Book review 375
Geach, G A *Formation of 'Hair Line Cracks' by Hydrogen introduced into Steel by Electrolysis* 98
Ghosh, J C (and M V C Sastri and K A Kini) *Mixed Adsorption of Hydrogen and Carbon Monoxide of Fischer-Tropsch Catalysts* 584
Gilbert, C L Book review 425
Gillis, J Rapid Analysis of Silicates 74
Gimingham, C T Colorado Beetle Problem 310
Glanville, W H Road Research Laboratory of the D S I R 514
Glueckauf, E Book review 283
Goddard, L S Book review 84
Goldie, A H R Book review 139
Goodwin, E T Book review 198
Goudsmit, S A Book review 183
Gourlay, J S *Shift of the Aromatic Band in Substituted Benzene* 242
Green, J R (and G H Harris) *A Mathematical Typewriter* 378
Gutfreund, H The Ultracentrifuge 442
Gutmann, V *Iodine Monochloride as an Ionizing Solvent* 337

Halsall, T G Book review 183
Hannah, M Book review 285
Hardwick, P J Book review 374

Italic type indicates original papers and communications in the Research Supplement

HARLAND, S C Book review 372
HARPER, R Psychophysical Relationships and their Study 350
HARRIS, G H (and J R Green) *A Mathematical Typewriter* 378
HASSEL, O (and E Amble) *Dipole Moment of 1,2,3,4,5,6-Hexachlorocyclohexane* 52
— (and K Lunde) $1\kappa,3\kappa,5\kappa$-('Cis') *Cyclohexanetriamine* 484
— Stereochemistry of *Cyclohexane* 504
HASZELDINE, R N *Perfluoro Amines* 430
HEERTJES, P M *Industrial Filtration* 254
— (and L J Revallier) *Some Properties of Nitrating Acids consisting of Nitric Acid and Sulphur Trioxide* 286
HEPPELL, H K (and J H Calderwood and R Cooper) *The Dielectric Properties of Copper Oxide Rectifiers* 530
HERDAN, G *Use of Inequalities in Polymer Research* 35
— *Index of Non-uniformity of Particle Shape* 385
HERINGTON, E F G *Thermodynamic Tests for Vapour-Liquid Equilibrium Data on Ternary Systems with Some Comments on Extractive Distillation* 41
— (and P B G Upton) *A Rapid Immersion Silvering Method of High Efficiency* 289
HEYMANS, C Chemoreceptors and Regulation of Respiration 355
HILL, R A W (and L L Sutton, R B Temple and A White) *A Study of Slow Self-propagating Reactions in Solids* 569
HIRST, W (and A W Crook) *Adhesion of Indium under Static and Dynamic Loading* 432
— (and J K Lancaster) *Estimation of the Surface Areas of Powders from the Temperature Dependence of Adsorption from Solution* 336
HOAR, T P (and K W J Bowen) *Low Temperature Ferromagnetism of Sigma Phase in an Alloy Steel* 484
HOHN, H Mercury in Chemical Metallurgy 16
— Applications of Amalgam Metallurgy 407
HOLTER, H Laboratories of the Carlsberg Foundation 274
— (and K Linderstrøm-Lang) Micromethods in Histochemistry and Cytochemistry 315
HOSELITZ, K Permanent Magnet Association Central Research Laboratory 77
HOWES, F N Honey and its Botanical Sources 127
HUGHES, A Book review 568
HUGHES, E D (and P B D de la Mare and C A Vernon) *Mechanism of Aromatic Halogenation, The Chlorine Cation,* Cl^+ 192
— — — *Reaction of Chlorine Cations with Olefins* 242
HUNTER, R F Carotenoids and Vitamin A 453

ISRAEL, J *The Blue Sun* 579
INGOLD, C T Book review 426

JEFFERY, G H (and J Leicester and A I Vogel) *Bond Refractions and Bond Parachor of the* C=N *Link* 190
JONES, R V (and W Paul) *Separation of Small Spheres According to Size* 98

KATZ, B Electrical Properties of Muscle Fibre 359
KAUFMAN, M *Improved Method for Precipitation of Polymers from Solution* 244
KELLY, H C Japanese Science and Technology 341
KENT, P W *Characterization of d-Glucosamine* 427
KINI, K A (and J C Ghosh and M V C Sastri) *Mixed Adsorption of Hydrogen and Carbon Monoxide of Fischer-Tropsch Catalysts* 584
KOLB, O K Book review 281
KOLBUSZEWSKI, J *Notes on the Deposition of Sands* 478
KUHN, W Book review 138

LALAND, S (and W G Overend and M Stacey) *Some Effects of the Ultrasonic Irradiation of Deoxyribonucleic Acids* 386
LAMPITT, L H Book review 93
LANCASTER, J K (and W Hirst) *Estimation of the Surface Areas of Powders from the Temperature Dependence of Adsorption from Solution* 336
LANDSBERG, P T Book review 567
LARKE, L W (and L Rotherham) *Creep Deformation of Metals* 434
LEEDY, H A Armour Research Foundation of Illinois Institute of Technology 27
LEICESTER, J (and A I Vogel) *New Method for the Preparation of as-Dialkyl Hydrazines, Bond Refractions and Bond Parachors of the* N—N *and* N=N *Links* 148
— (and G H Jeffery and A I Vogel) *Bond Refractions and Bond Parachor of the* C=N *Link* 190
LINACRE, E *Heat Transfer by Spray Cooling* 429
LINDERSTRØM-LANG, K (and H Holter) Micromethods in Histochemistry and Cytochemistry 315
LINDLEY, H Recent Advances in Knowledge of Wool Structure 509
LONG, L H *Valence States of Carbon and the Heats of Dissociation of* CO, CN *and* N_2 291
LONSDALE, K Specialized Scientific Training and Citizenship 437
LOUDON, J D (and J C Speakman) *The Solubility of Colchicine in Water* 583
LULLA, B S *Initial Increase in Viscosity during Action of Bacterial Amylase on Starch* 290
— *Penicillin Production with Lucerne* 581
LUNDE, K (and O Hassel) $1\kappa,3\kappa,5\kappa$-('Cis') *Cyclohexanetriamine* 484

MADDAMS, W F (and R Schnurmann) *Ultraviolet Absorption Spectra of the Two Phenylnaphthalenes* 191
MADDOCK, A G Book review 473
MALEWSKI, A M *New Formulae for Double Refraction in Liquids* 240
MARÉCHAL, A (and P Fleury) Institut d'Optique Théorique et Appliquée, Paris 176
MASON, I L Livestock Breeding Research 171
MASSART, L (and G Peeters) Artificial Lactation and Perfusion of the Bovine Mammary Gland 217
MATHEWS, S *Envelopes of Oil Drops Suspended in Glue Solution* 86
— Interfacial Tension of Medicinal Paraffin/Water 225
MEARA, M L Book review 330

Italic type indicates original papers and communications in the Research Supplement

MEGSON, N J L Book review 374
MENTER, J W *Effect of Temperature on Lateral Spacing of Fatty Acid Monolayers on Metals—an Electron Diffraction Study by Transmission* 381
MERRINGTON, A C (and E G Richardson) *Obscuration and Smoke Density* 526
MILLAR, A R Book review 471
MOORE, H Book review 282

NASLUND, M Forest Research Institute of Sweden 320
NEWTH, F H (and L I Wiggins) *2,5-Bishydroxymethylfuran* 50
NIXON, I S (and G Raumann and K G Denbigh) *Transition between Laminar and Turbulent Flow in Various Liquids* 520

OLNEY, M J (and G C Smith) *Surface Effect Occurring on High Carbon Steels Heated and Cooled in Vacua* 194
OVERBECK, C J Sound Writing and Reading 268
OVEREND, W G (and M Webb) *Nucleic Acids Relationship between Ribo- and Deoxyribonucleases* 238
— (and S Laland and M Stacey) *Some Effects of the Ultrasonic Irradiation of Deoxyribonucleic Acids* 386

PAUL, W (and R V Jones) *Separation of Small Spheres According to Size* 98
PARTINGTON, J R Book review 181
PATERSON, S *One dimensional Flow behind a Steady Plane Detonation* 99
PEETERS, G (and I Massart) Artificial Lactation and Perfusion of the Bovine Mammary Gland 217
PETHICA, B A (and E R Roberts and E R S Winter) *The Hydrogenase of Azotobacter* 382
PHILLIPS, D C *Crystal Structure of l-Ephedrine Hydrochloride and Hydrobromide* 388
— *Crystal Structure of Acridine III* 578
PIRANI, M Development and Application of High Vacuum Technique 540
POLLETT, W F O *Elastic Thixotropy* 483
PORTER, A Some Applications of Servomechanisms 166
PRATT, J S COURTNEY *A Cleavage Step on Mica with a Height that is a Half-integral Multiple of the Crystal Lattice Spacing* 47
PRIME, H A *Emission of Infra-red Radiation by Metallic Powders* 51

QUENOUILLE, M H Experimental Design 213

RAO, S K SREEPATHI (and M K Subramaniam) *Gene Mutations Induced by Camphor in Yeast* 49
RAUMANN, G (and I S Nixon and K G Denbigh) *Transition between Laminar and Turbulent Flow in Various Liquids* 520
RAYNOR, G V (and R L Berry and M B Waldron) *Outer Brillouin Zones for the Face-centred Cubic, Body-centred Cubic and Close Packed Hexagonal Structures* 195
REINER, M Book review 227
— (and I Braun and H Frey) *Mechanism of the Weissenberg Effect* 243
REVALLIER, L J (and P M Heertjes) *Some Properties of Nitrating Acids consisting of Nitric Acid and Sulphur Trioxide* 286
RHODES, A (and W A Sexton, L G Spencer and W G Templeman) *Use of Isopropylphenylcarbamate to Reduce Sprouting of Potato Tubers During Storage* 189
RICHARDSON, E G (and A C Merrington) *Obscuration and Smoke Density* 526
RICHARDSON, H O W (and A N Barker and N Feather) *An Emission Microscope for Photoelectron Radiography* 431
RIDDELL, G L The Printing, Packaging and Allied Trades Research Association 465
RIGG, Sir THEODORE Cawthron Institute, Nelson, New Zealand 131
ROBERTS, E R (and B A Pethica and E R S Winter) *The Hydrogenase of Azotobacter* 382
ROBERTSON, R H S (and J M Fletcher) Fluorine and Teeth 23
ROBINSON, A Book review 373
ROTHERHAM, L (and L W Larke) *Creep Deformation of Metals* 434
ROUGHTON, F J W Book review 329
RYGH, O *Causes of Dental Caries* 193
— *Determination of Natural Sources of Vitamins D* 577

SASTRI, M V C (and J C Ghosh and K A Kini) *Mixed Adsorption of Hydrogen and Carbon Monoxide of Fischer-Tropsch Catalysts* 584
SAYERS, J Book reviews 284, 371
SCHNURMANN, R (and W I Maddams) *Ultraviolet Absorption Spectra of the Two Phenylnaphthalenes* 191
SCHULMAN, J H Book review 567
SEXTON, W A (and A Rhodes, L G Spencer and W G Templeman) *Use of Isopropylphenylcarbamate to Reduce Sprouting of Potato Tubers During Storage* 189
SHOOTER, K V (and F P Bowden) *Frictional Behaviour of Plastics Impregnated with Molybdenum Disulphide* 384
SHOPPEE, C W Book review 472
SMITH, G C (and M J Olney) *Surface Effect Occurring on High Carbon Steels Heated and Cooled in Vacua* 194
SMITH, K M *A New Virus Affecting Mangolds, Sugar-beet and Related Plants* 434
SONDHEIMER, E H Book review 138
SPEAKMAN, J C (and J D Loudon) *The Solubility of Colchicine in Water* 583
SPENCER, L G (and A Rhodes, W A Sexton and W G Templeman) *Use of Isopropylphenylcarbamate to Reduce Sprouting of Potato Tubers During Storage* 189
SPRINGALL, H D Heat of Atomisation of Carbon 260
SREEPATHI RAO, S K (and M K Subramaniam) *Gene Mutations Induced by Camphor in Yeast* 49
STACEY, M (and S Laland and W G Overend) *Some Effects of the Ultrasonic Irradiation of Deoxyribonucleic Acids* 386
STAKMAN, E C Science and its Sphere of Influence 101
SUBRAMANIAM, M K (and S K Sreepathi Rao) *Gene Mutations Induced by Camphor in Yeast* 49
SUMMERVILLE, W A T Water Erosion 547

Italic type indicates original papers and communications in the Research Supplement

Sutton, L E (and R A W Hill, R B Temple and A White) *A Study of Slow Self-propagating Reactions in Solids* 569

Taylor, A M (and J F Archard and P L Clegg) *Photoelectric Methods for Metal Optics* 339
Taylor, G I Defence Services Research Facilities 34
Temple, R B (and R A W Hill, L E Sutton and A White) *A Study of Slow Self-propagating Reactions in Solids* 569
Templeman, W G (and A Rhodes, W A Sexton and L G Spencer) *Use of Isopropylphenylcarbamate to Reduce Sprouting of Potato Tubers During Storage* 189
Tetlow, K S *Azobenzene Part II Infra-red Spectra of Slurries of Cis- and Trans-azobenzene* 187
Turnbull, H W Mathematics in the Larger Context 197
Tustin, A Progress in Manual and Automatic Control Apparatus 245

Ubbelohde, A R Higher Education for Technologists 53
— Activation Processes in the Sensitiveness of Explosives 207
— (and W M Evans) *Formation of Munroe Jets and their Action on Massive Targets* 331
— (and W M Evans) *Some Kinematic Properties of Munroe Jets* 376
Upton, P B G (and F F G Herington) *A Rapid Immersion Silvering Method of High Efficiency* 289

van Krevelen, D W Gas Absorption 106
Vernon, C A (and P B D de la Mare and E D Hughes) *Mechanism of Aromatic Halogenation The Chlorine Cation,* Cl+ 192
— — — *Reaction of Chlorine Cations with Olefins* 242
Vogel, A I Book review 183
— (and J Leicester) *New Method for the Preparation of as-Dialkyl Hydrazines Bond Refractions and Bond Parachors of the* N—N *and* N=N *Links* 148
— (and G H Jeffery and J Leicester) *Bond Refractions and Bond Parachor of the* C=N *Link* 190

Waddington, C H Book review 228
Waldram, J M Book review 33
Waldron, M B (and R L Berry and G V Raynor) *Outer Brillouin Zones for the Face-centred Cubic, Body-centred Cubic and Close Packed Hexagonal Structures* 195
Ward, E R (and L A Day) *Relation between Structure and Melting Point in Aromatic Compounds* 580
Wardlaw, W (and D C Bradley) Orthoesters of Silicon, Titanium and Zirconium 462
Webb, M Gram Staining Reaction for Micro-organisms 113
— Book review 184
— (and W G Overend) *Nucleic Acids Relationship between Ribo- and Deoxyribonucleases* 238
Wexler, Aaron Superconductivity 534
Weyl, W A *Crystal Chemical Considerations of the Surface Chemistry of Silica* 230
White, A (and R A W Hill, L E Sutton and R B. Temple) *A Study of Slow Self propagating Reactions in Solids* 569
Wiggins, L F *Preparation of Levulinic Acid Use of Sodium Levulinate* 140
— (and F H Newth) *2,5-Bishydroxymethylfuran* 50
Wight Bakke, E Research and Practice in Industrial Relations
Wilhelm, R H *Fluidization of Masses of Particles* 159
Wilson, A J C *X-Ray Determination of Mirror Planes and Rotation Axes* 48
— *Note on Diffraction by a Dislocation* 387
— Study of Imperfect Crystals by Powder Photographs 394
Wilson, C G *Note on the Emission of Positive Ions from Heated Glasses* 577
Winter, E R S (and B A Pethica and E R Roberts) *The Hydrogenase of Azotobacter* 382
Wright, W D Book reviews 284, 564
Wunderly, C *A Simple Method for Measuring the Movement of Insoluble Monolayers at Air/Water Interface* 531

Youd, C S Book review 329
Young, J Z Book review 282
Young, L (and F P Bowden) *Influence of Interfacial Potential on Friction and Surface Damage* 235

Zucker, F J Mathematics in the Larger Context 326
Zwikker C Absorption of Sound by Porous Materials 400

Italic type indicates original papers and communications in the Research Supplement

Name Index

Aamodt, L G 497
Abbot, D A 547
Abel, F 122, 126
Abeles, F 179
Abelson, P H 432
Abraham, E P 582
Adam, N K 90, 337
Adams, B A 447, 452
Adams, D P 85
Adams, G 326
Adams, H T 34
Adams, J C 86, 90
Adams, W S 279
Adamson, A W 452
Adamson, D W 124, 126
Addinall, C R 420
Adkins, H 465
Adrian, E D 31
Agnew, L R C 224
Ahmad, B 461, 504
Aitchison, L 31
Albert, A 147
Albouy, G 196
Alexander, A. E 90, 525, 532
Alexander, P 68, 73, 512, 542
Alexander, T 342
Allen, J E 528
Allen, J F 540
Alliott, E A 256, 259
Almy, C 259
Ambrose, E. J 513
Ambrose, P M. 417
Amble, E 52
Amelin, A G 287
Ammann-Brass, H 196
Andersen, A C 320

Andersen, H C 267
Andersen, P 484, 509
Anderson, C T 417, 547
Anderson, J G C 135
Andrade, E N da C 32, 181, 237, 434, 436, 525, 542
Andre, G 142, 145
Andreas, J M 86, 90
Andres, D 46
Andresen, N 279
Andrew, E R 539
Andrew, J H 98
Andrew, W 228
Andrewes, C H 424
Andrews, D H 539
Anfinsen, C B 315, 320
Anger, V A 557
Anitchkov, S V 359
Antoniani, C 503
Antweiler, H J 23
Appleyard, E T S 538, 540
Araki, T Z 358
Archard, J F 340
Arens, F J 453, 458, 461, 504
Argles, G K 249, 253
Armitage, F D 470
Arndt, K 122, 126
Arnulf, A 178, 180
Arroe, O H 497
Artom, A 503
Ashby, E 31
Ashley, E 226
Astbury, W T 11, 364, 509, 513
Astrup, T 279
Atkins, B R 547
Auerbach, C 50
Aufricht, H 557
Aulin-Erdtman, G 63, 67
Avery, D G 542, 547
Avery, O T 119
Awapara, J 499, 503
Ayrton, W E 342

Baader, J 336
Babkin, B P 180
Bachman, C H 371
Bächle, O 463, 465
Backström, H 196
Baer, J E 147
Bagguley, D M S 497
Bagnold, R A 31, 483
Bai, M Prema 50
Bain, A 150
Bain, J W 259
Baker, E M 43, 46
Baker, E P 259
Baker, F 225
Baker, J R 151
Baker, W 126
Baker, Z 120
Barke, E Wight 5
Balachowsky, A 314
Baldwin, E H 83
Ball, S 461
Bamann, E 319
Bamberger, E 126
Bamford, G H 513
Bammann, J 126
Banks, F R 370
Banks, M A L 280
Banks, W H 289, 530
Banta, A M 50
Barbieri, J 126
Bardeen, J 497
Barkas, W 97
Barker, A N 432
Barker, G C 235, 237
Barker, K H 450, 452
Barlow, H E M 83
Barnard, M M 215, 217
Baron, M 355
Bartell, F E 90
Bartholomew, J W 114, 119
Bartlett, F C 354
Bartlett, P D 125, 127, 159
Barton, D H R 279
Barua, R K 503
Bashforth, F 86, 90
Basset, J 266
Bastiansen, O 52, 508
Bastow, S H 83, 237
Bates, L F 180
Bateson, W 171
Batson, R G 184
Bauer, L 147
Bauer, O 557
Bauer, W C 161, 164, 259
Bauman, W C 452
Baumann, C A 502, 504
Baumann, H 327
Baumfeld, L 557
Baver, L D 549
Bawn, C E H 40
Beadle, L C 319
Beakbane, A B 253
Bear, R S 360, 511, 513
Beaujard, L 436
Beaver, S H 135
Becker, R 77, 82, 285
Becks, H 27
Bedson, S P 424
Beeck, O A 519
Beevers C A 10
Behr, A 73
Beilin, R 350
Bell, J 171
Bell, R P 570, 576
Bencze, B 500, 503
Benedict, M 46
Benham, G H 498, 503
Bennati, D 359
Benneck, H 98
Bennet-Clark, T A 31, 180
Bennett, H H 547, 550
Bennett, M C 31, 519
Bensley, R A 315
Bente, F 140, 145
Benton Jones, Sir Walter 280
Beranek, L L 407
Berg, G 22
Berg, G A 67
Berg, R 552, 557
Berg, W F 96, 478
Bergmann, L 73
Bergmann, M 239, 513
Beringer, R 492, 497
Berkhout, H W 500, 503
Berkofer, L 145
Bernal, J D 9
Bernthal, T 359
Berriman, R W 196
Berry, R L 196
Bersin, T 464
Bertaud, F 399
Berthelot, M 121, 126, 142, 146, 265, 267
Berthollet, C L 149
Berzelius, J J 121, 126, 462, 465
Bessemer, A 314
Bessey, O A 317, 320, 503
Bethe, H A 497, 567
Beuthe, H 73
Beuttenmüller, E 73
Beveridge, W I B 424
Bhatnagar, S S 291
Bible, N N 259
Bichowsky-Stournitzky, L 120
Bickerton, R L 280
Bickoff, E M 504
Bigelow, L A 339
Biggar W A 225
Bijvoet, J M 52, 508
Bilicke, C 508
Billings, H 375
Binkley, R C 417, 420
Binnie, A M 520, 525
Bichowsky, F R 267
Birch, R E 309
Birch-Andersen, A 279
Bird, L H 503
Birkhoff G 336
Bischoff, F 465
Bishop, A W 483
Bishop, G H 259, 365
Bisson E E 383
Björkman, A 67
Bjurstedt, H 357, 359
Blachman, N M 398
Black, A N 327
Blackburn, S 512
Blackett, P M S 135, 183
Blackman, G E 31, 190
Blair, G W Scott 227, 355
Blanchard, A A 122, 126
Blanksma, J J 145
Blasius, H 520, 523, 525
Blaxter, K L 176
Bleaney, B 180, 490, 493, 497
Block, R J 509, 513
Bloomfield, A L 255, 259
Blottiau, F 179
Blout, E R 374
Blyth, F G H 483
Boas, W 83, 399
Boczkowska, M 314
Böeseken, J 122, 127, 507
Boell, E J 316, 320
Böttger, I 240
Bogue, J Y 359
Bohme, H 147
Bohren, B B 503
Boissonnas, C 196
Boivin, A 115, 119
Bollenbach, H 553, 557
Bolton, K 545
Bone, W A 100
Bonhoeffer, K F 231, 234
Bonilla, C F 259
Bonner, J 252
Bonnier, G 176

Booth, A D 7, 12
Booth, V H 497, 500, 503
Borg, A F 120
Boring, E G 355
Born, M 200, 471, 540, 567
Borodastova, Z B 287
Borrow, A 316, 320
Bos, A 501, 503
Bose, A K 98
Bottelier, H P 315, 320
Botwright, W E 120
Bouckaert, J J 359
Bouma, P J 284
Bouman, J 399
Bowden, F P 48, 148, 212, 235, 237, 384, 425, 433
Bowden, K 147
Bowen, E J 520, 525, 576
Bowen, K W J 484
Bowman, J 165
Boyd, E 532
Boyd, G E 452
Boyd Orr, Lord 375
Boyer, P D 503
Boyle, P J 364
Boys, S F 570, 576
Bozler, E 364
Braby, F C 136
Brace, P H 547
Brachet, J 316, 320
Bradfield, A E 193
Bradford, F C 250, 253
Bradley, A J 80, 280, 399
Bradley, D C 462
Bradley, R S 307, 309
Brándli, H 330
Bragg, J K 497
Bragg, Sir William 6, 439
Bragg, Sir Lawrence 6, 11, 48, 230, 235, 399
Brandsma, W I 122, 127
Braude, E A 147
Braun, I 244, 483
Braun, J V 140, 145
Braverman, J B S 33
Brearley, A 285
Breckenridge, R G 531
Bredee, H L 257, 259
Breny, R 314
Breslow, D S 159
Bretscher, L 461, 568
Brew, W 503
Brewer, L 266
Brewster, Sir David 298
Bridges, C B 229
Bridgman, P W 135
Bridgman, W B 447
Brieghel-Muller, A 258
Briegler G 241
Bright, N F H 185, 188
Brillouin, L 195
Brimble, L J F 31
Brindley, G W 399
Brink, N G 422, 424
Bristow, J R 540
Broad, D W 97
Brock, M J 503
Brockmann, H 454, 461
Brodtkorb, T 142, 145
Brönsted, J N 182
Broeze, J J 327
Brogan, D W 183
Brooe, J A 504
Bromehead, C N 27
Brooks, B T 426
Brown, A E 513
Brown, A E C 302, 328
Brown, C B 550
Brown, G L 31
Brown, G P 547
Brown, G S 170
Brown, M J 97
Brown, W 355, 463, 465
Browne, E T 31
Brownell, L E 257, 259
Brownlee, K A 217
Bruel, D 319
Brummage, K G 382
Brundrett, F 82
Bruneteau, J 314
Bruns, H 41
Brunt, Sir David 31, 83
Bryden, C L 259
Buchanan, R E 176
Buchanan-Smith, A D 173, 176
Buchheim, S 241
Buchholz, E 557
Buchthal, F 365
Bürgen, M 248, 253
Bu he, W 259
Bugie, E 424
Bulian, W 184
Bull, H B 513, 532
Bunce, A C 549
Bunn, C W 11
Burch C R 541, 547
Bureau, M 348
Burg, A B 497
Burhop, E H S 31
Burk, R E 159, 283, 519
Burkill, J C 83
Burman, J P 216
Burmeister, L 259
Burn, G P 364
Burnet, F M 135
Burris, R H 382
Burton, E F 540
Burton, H 141, 145
Burton, M 297, 471
Burton, P C 196
Burwell, R L 159
Bush, V 171
Busnel, R G 314
Butler, J A V 229, 387, 489
Butler K 119
Butterfield, H 485

Cadman, C H 252
Cadman, G O 119
Cady, H P 338
Cahn, R W 436
Calbert, C E 504
Calderwood, J H 531
Caldwell, S H 171
Callan, H G 327, 565
Calvin, M 229
Cama, H R 499, 503
Cameron A T 355
Cameron, D H 580
Campbell, D P 170
Campbell, E C 139
Campbell, I E 547
Campbell, W G 375
Candler, C 184
Carathéodory, C 375
Carey, C F 280
Carl, R 212
Carlisle, C H 9, 12
Carmack, M 146
Carman, P C 255, 259
Carman, W C 547
Carpenter, F H 238, 240
Carroll, B H 196
Carson, E M L 267
Carson, T 185, 188
Carter, C E 240
Carter, E G H 512
Cartwright, N J 63, 67
Casimir, H B G 537, 539
Caspersson, T 315, 319
Cassie, A B D 135, 513
Cathcart, W H 558, 562
Cauchy, A L 40, 85
Cavanillas, L 365, 369
Cave-Brown Cave, T R 327
Cavendish, H 85
Cawley, J D 460
Cawthron, I 131
Cecil, R 446
Chaboussou, F 314
Chaddock, R E 46
Chadwick, Sir James 135
Chain, E 119
Chaix, M 147
Challenger, F 280
Chalmers, B 32, 339
Chambers, H H 547
Chambers, L 69, 73
Chambers, L A 387
Chance, B 84
Chandi ff, G C 552, 557
Chandler, W H 249, 251, 253
Chandrasekhar, S 34, 83
Chang, W T 249, 253
Chantrenne, H 240, 278
Chapman, S 139
Chapman-Andresen, C 279
Chappellier, A 314
Chaptal, J A C 149
Chargaff, E 238, 240
Charlot, G 374
Charpy, G 150
Charrington, Sir John 226
Chatt, J 580
Chatterjee, A 504
Cheeseman, G W H 461
Cheesman, E E 12, 16
Cheng, G K 547
Cheng, K C 540
Cherry, C 84
Cherton, R 267
Chesters, J H 303, 307, 309
Chevalier, M 314
Chevenard, P 153
Chilcote, M E 499, 501, 503
Chisholm, B 441
Cholnoky, L 557
Christensen, L K 278
Christiansen, J B 499, 503
Churchill, E S 120

Churchman, J D 114, 119
Claesson, S 452
Claff, C L 316, 319
Clark, A M 42, 46
Clark, E T 350
Clark, J 237
Clark, R H 120
Clarke, A C 329
Clarke, B W 255, 259
Claude, A 315, 319
Clausing, P 186
Clausius, R J E 391
Clayden, E G 184
Clayton, E H 370
Clayton, J 181
Cleeton, C E 492, 497
Clegg, P L 340
Clements, F H 309
Cline, J K 421, 424
Coates, A C 196
Coblentz, W W 350
Cochran, W G 217
Cochrane, W 10
Cockburn, R 513
Coffman, D D 145
Cohan, L H 97
Cohen, V W 497
Cohen Henriques, P 509
Cohn, W E 452
Coker, E G 303
Colbert, J B 151
Colburn, A P 41, 46
Cole, F J 135
Cole, K S 364
Cole, L C 558, 562
Coles, D K 497
Collier, G W 549
Collins, A M 145
Collins, F D 461
Combes, C 336
Commoner, B 318, 320
Comrie, I T 180
Comroe, J H 357, 359
Conant, J B 125, 127, 159
Connet, H 358
Conrad, M 145
Considen, R 510, 513, 554, 557
Conway, E J 360, 364
Cook, A H 185
Cook, G H 447
Cook, J W 280, 584
Cook, M 196, 399
Cook, R 224
Cook, W H 559, 562
Cooke, P W 12
Cooke, R G 285
Cooley, M L 499, 503
Coombes, A I 503
Cooper, R 591
Copp, J L 212
Coppen, F M V 355
Coppock, J B M 558, 562
Corak, W S 536, 539
Corey, R B 12
Cori, C F 279
Corley, R S 374
Corner, E J H 426
Corner, J 570, 576
Cornford, S J 558
Cornog, J 338
Correns, C W 229
Cosslett, V E 566
Coster, H M 287
Cottrell, A H 31
Cottrell, T L 188
Couffignal, L 177, 180
Coulson, C A 156, 159, 180, 579
Coulson, E A 46
Coumoulos, H 27
Coupe, R R 530
Courant, R 373
Courtney-Pratt, J S 48
Cousin, H 63, 67
Coussens, R 221
Couturier, A 314
Cowan, S L 365
Coward, K H 502, 504
Cowley, J F 126
Cox, D R 285
Cox, E G 9, 425
Cox, L R 180
Coxeter, H S M 180
Coxon, G H 280
Crafts, J 462, 465
Craggs, J D 138, 528, 564
Craik, K J W 355
Crampton, F W 176
Crandall, J B 403, 407
Crane, M B 253
Creed, R H 460
Cresswell, W T 148
Crew, F A E 171
Crook, A W 340, 433
Cross, A H 483
Crossland, L B 560, 562
Crowfoot, D 9, 12
Croze, F 178, 180
Crump, L M 373
Crussard, G 436
Csonka, F A 509, 513
Cubiles, R 240
Cullen, G E 119
Cummings, J N 176
Cunningham, G H 180
Curie, J 68
Curie, P 68
Curran, S C 564
Curtis, H J 365
Curtis, L 183
Curtis, W E 424
Cushnie, G 225
Cuthbertson, D P 222, 225
Cuthbertson, W R 513
Cuthill, J C 186
Cymerman, J 147

Dackerman, M E 315, 320
Dailey, B P 496
Dailey, D I 176
Dainton, F S 327
Dale, Sir Henry 136, 365, 420, 424
Dalling, I 424
Damerell, V R 283
Daniel, V 399
Danielli, J F 31, 90, 364
Dann, W J 498, 503
Danó, M 509
Darapsky, L 259
Darcy, H P G 259
D'Arcy Thompson, Sir 327
Darling, S 279
Darlington, C D 34, 229, 565
Darmois, G 178, 180
Darwin, Sir Charles 486
Daunt, J G 537, 539
Dautrebande, L 359
Dauvillier, A 259
Davenport, H 31
Davey, A 336
Davey, D G 31
David, F N 31
Davies, B L 372
Davies, C W 447, 452
Davies, E R 425
Davies, G I 193
Davies, K N 196
Davies, O L 217
Davies, R O 59, 62
Davis, H 355
Davis, K H 274
Davoll, J 239
Davson, H 90
Day, H G 577
de Boer, J H 472
de Broglie, L 326
de Bunsen, B 181
de Graaf, J E 280
de Gramont, A 177
de Gorter, B 417, 420
de Haas, W J 540
de la Mare, P B 193, 243
de Martonne, E 226
de Robertis, E D P 228
de Wael, J 382
de Wilde, J 314
de Witt, C C 257, 259
de Witt, J B 503
de Wolff, P M 399
Dean, H T 23, 27
Dean, R B 364
Dean, R S 416
Dearing, A 462, 465
Deatherage, C F 27
Debot, R 91, 96, 474, 478
Debye, P 41
Dehlinger, U 399
Delaporte, B 117
Demarcq, J 179
Denbigh, K G 393, 520
Derby, J V 503
Derbyshire, A E 193
Deriaz, R E 145, 239
Derleth, C P 259
Dermen, H 50
Dermer, O C 145
Dermer, V H 145
Derry, L W 135
Dervichian, D G 532
Descartes, R 486
Desirant, M 539
Desvignes, F 179
Deuel, H J 456, 461, 499, 503
Deuel, J 461
Deussen, E 114, 119
Devine, J 461
Devons, S 31, 568
Dewar, M J S 134, 159, 181
Diamond, C 372
Diamond, H 347, 350
Dick, J S 376

Dickerson, G E 173, 176
Dickey, G D 259
Dickinson, R G 308
Dietrich, G 65
Dilworth, C 196
Dinardo, A 547
Dingle, E 227
Dirac, P A M 391
Ditlevsen, E 279
Dittrich, M 553, 557
Diver, C 31
Divers, E 342
Dixmeras, M 314
Doan, R L 349
Dobson, G C 530
Doby, G 63, 67
Dobzhansky, T 50
Dodd, E C 196
Dodé, M 287
Doetsch, G 330
Doming, C E 549
Donald, H P 176
Donald, M B 255, 259, 280
Donat, J 259
Donell, J W 259
Doniger, R 240
Dorey, S F 226, 370
Doring, W 82
Doty, P M 41
Doub, L 147
Douch, E J H 171
Douglas, A M B 280
Douglas, H W 225
Dourneau, F 179
Downs, J C 417
Doxey, D 190
Doyle, W L 279
Drake, C F 583
Draper, M H 364
Drucker, B 513
Drumm, P J 123, 127
Drummond, J C 454, 456, 461
Drury, A N 326, 424
du Vigneaud, D 422, 424
du Vigneaud, V 509, 513
Dubos, R J 114, 119, 422, 424
Duché, J 373
Duckworth, J 225
Duclaux, J 259
Dudding, B P 425
Dudley, H 272, 274
Duke, F R 552, 557
Duley, F L 549
Duncan, J F 452
Duncan, W J 31
Dunham, H H 50
Dunitz, J D 6, 9, 12
Dunmore, F. W 347, 350
Dunn, C L 41, 46
Dunn, E 314
Dunn, H K 274
Dunnington, P G 528
Dunstan, A E 426
Dunstan, E J 280
Dunworth, J V 565
Durnford, J 528
Dushman, S 543, 547
Dyatkina, M F 34, 139
Dyer, H 342
Dymond, E G 345, 350
Dyson, G M 229
Dyson, T A 185, 188

Eales, N B 375
Earl, J C 120, 125, 127
Easterfield, Sir Thomas 131
Ebelmen, A 462, 465
Eccles, J C 364
Eckman, D P 170
Eddington, Sir Arthur 227
Eden, E 503
Edisbury, J R 461, 498, 500, 503
Edison, T A 235, 237
Edlen, B 267
Edmunds, I G 399
Edsall, J T 386
Edwards, H D 497
Edwards, O S 399
Eeckhout, J 74
Ege-Larsen, N 278
Ege, R 358
Eger, G 22
Egerton, Sir Alfred 185
Egeter, H 259
Eggert, J 196
Ehrensvard G 279
Ehret, L 73
Eichhorn, J 452
Einstein, A 184, 389
Ekstein, H 399
Elford, W J 180
Elgin, J C 165
Ellefsen, Ø 52, 508
Ellenberger, H A 499, 501, 503
Ellinger, G M 225
Elliott, G D 309
Ellis, W J 510, 513
Ellison, W 58
Ellison, W D 548, 550
Elöd, E 512
Elsden, S R 225
Elsey, H M 338
Ely, F 219, 221
Ely, R 500
Embree, N D 460
Emeléus, H J 32, 328, 338, 426, 431, 472
Emerson, G A 422, 424
Emerson, O H 422, 424
Emert, O 22
Engel, C 501, 503
Engelhard, E 207
Engle, E T 176
Engström, A 320
Ennis Jr, W B 190
Epstein, L A 119
Erdtman, H 63, 67
Ergun, S 165, 257, 259
Erlanger, J 365
Erlenmeyer Jr, E 145
Errera, J 259
Eskedal, H W 176
Esmarch, W 547
Etcheverry, H 557
Eucken, A 259
Evans, H M 422, 424
Evans, J W 31
Evans, W M 331, 376
Evelyn, K A 503
Evenari, M. 253
Evershed, S 82
Eversole, W G 113
Ewald, P P 399
Ewan, N A 503
Ewert, R H 41
Ewing, J A 342
Eyring, H 109

Faber, W 314
Fabry, C 149, 177
Fagan, T W 59, 62
Fahraeus, R 442
Fahrenhorst, E 184
Fairbrother, F 159
Fajans, K 230, 235, 267
Falconer, D S 173
Falla, L 478
Falmouth, the Right Hon the Viscount 370
Faltings, K 267
Faraday, M 440
Faraggi, H 196
Farber, L 165
Farber, S 359
Farmer, E H 330, 547
Farnell, G C 196
Farrant, J 511, 513
Fatt, P 364
Favor, H H 560, 562
Fawcett, E W M 547
Fawcett, H S 253
Fayol, H 149, 153
Feachem, C G P 340
Feather, N 432
Fechner, G T 352, 355
Federico, L 509
Fedorov, B F 33
Fehnel, E A 147
Feigl, F 550, 552, 557
Feigl, H E 557
Feiner, R R 119
Feldberg, W 365
Fenn, W O 364
Fermi, E 279
Fernberger, S W 355
Fernholz, E 422, 424
Feuell, A J 73
Feytaud, J 314
Fialkov, Ya A 337
Fieser, L F 192
Fildes, Sir Paul 135
Filewicz, W 250, 253
Filon, L N G 303
Fink, R M 330
Finkelstein, J 422, 424
Finney, D J 216, 352, 355, 564
Fischer, A 279, 327
Fischer, E 145
Fischer, F G 240
Fisher, R A 172, 213, 215, 217
Fisher, W A P 284, 298, 328
Fiske, J 105
Fizeau, A H L 176
Flagg, J F 557
Fleming, A 120
Fletcher, H 355
Fletcher, H F 274
Fletcher, J M 23
Fleury, P 176, 180
Flückiger, E. 67

Flosdorf, E W 387, 547
Flowers, J W 528
Folkers, K 421, 424
Fono, A. 239
Fordham, S 90
Forland, T 234
Forrester, G P 339
Forster, F 120, 126
Foster, A G 97, 279
Foucault, J B L 85, 176
Foundaminsky, I J 408, 417
Foust, H C 165
Fowler, P H 196
Fowler, R D 540
Fowler, W A 226
Fox, C 330
Fox, J J 147
Foy, J R 502, 504
Fram, P 374
Frampton, V L 386
Francis, T 119
Françon, A 178
Frank, A H 176
Franzinetti, C 85
Fraps, G S 504
Fraps, R M 176
Fraser, H J 257, 259
Fraser, R P 100
Frazer, A C 90
Fredericq, E 278
Fredericq, L 356, 358
Freeth, F A 280
French, N R 271, 274
Frenzel, K 73
Fresnel, A J 176
Freud, S 488
Freudenberg, K 63, 67, 465
Freundlich, M 72
Frey, H 244, 483
Friauf, J B 100
Friedel, C 462, 465
Friedel, G 48
Friedel, R A 192
Friedensburg, F 22
Friedlander, G 473
Friedrich, W 6
Friedrichs, K O 373
Frisch, O R 473
Frocht, M M 283, 303
Fröhlich, H 51, 202, 207
Frumkin, A 237
Funk, H 464
Fuoss, R M 125, 127
Furberg, S 509

Gadsby G N 339
Garde, W 541, 547
Gage, J C 386
Gage, J G 386
Gaines, N 69, 73
Gale, E F 118
Galkin, A 540
Galton, Sir Francis 41, 171
Galvani, L 486
Ganguly, J 498, 503
Gans, R 336
Gardner, G S 44
Garner, F H 329
Garner, R J 248, 253
Garner, W. E 137
Garton, C G 372
Gasser, H S 365
Gates, S B 180
Gauss, K F 85
Gaydon, A G 261, 264, 267, 375
Gayet, R 359
Gay-Lussac, J L 149
Geach, G A 98, 280
Geiger, A 461
Geiger, W B 511, 513
Gemmell, A R 135
Gerard, R W 365
Gerding, H 288
Germer, L H 382
Gernandt, E 359
Gerö, L 264, 267
Gerretsen, F C 62, 374
Gerris, C 314
Gersh, I 315
Gershinowitz, H 264, 267
Geschwind, S 497
Gesell, R 356, 358
Getting, G A 27
Ghosh, J C 584
Gibbs, J W 85
Gibson, A 314
Gibson, A H 521, 525
Gibson, C S 181
Gibson, G P 499, 503
Gilbert, A 239
Gilbert, C L 425
Gilbert, H L 547
Gilbert, L A 387
Giliam, A E 460
Gilles, P W 266
Gillespie, J M 510, 513
Gillespie, R J 193
Gilliam, O R 496
Gilliland, E R 109, 113, 161, 164, 259
Gillis, J 12, 74
Gilman H 147
Gilson, A S 365
Gimingham C T 310
Ginsborg, B L 470
Ginsburg, V 540
Glanville, W H 514
Glasstone, S 584
Glesinger, E 375
Glick, D 275, 315, 319
Glockler, G 263, 267
Glover, J 503
Glover, R E 424
Glueckauf, E 283, 450, 452
Goddard, L S. 85
Godden, W 225
Godley, P 547
Goebel, W E 119
Golden, S 497
Goldfinger, P 267
Goldie, A H R 139
Goldschmidt, H J 280
Goldschmidt, V M 230
Goldstein, R F 425
Goldstein, S 327, 525
Golfman, M S 287
Gollwitzer-Meier, K 359
Gombás, P 85
Gomori, G 315, 319
Gonser, B W 547
Good, W E 492, 497
Goodeve, Sir Charles 466, 470
Goodman, B 331
Goodwin, E T 198
Goodwin, T W 461, 499, 503
Goppelsroeder, F 553, 557
Gordon, A H 279, 510, 513, 557
Gordon, Lord Dudley 153
Gordon, G S 159
Gordy, W J 494, 496
Gorodetskaja, A 237
Gorter, C J 537, 539
Gosner, B 388
Goto, H 553, 557
Goudsmit, S A 184
Goulden, C H 217
Gourlay, J S 242, 547
Graham, J 365
Graham, W 31
Gram, H C J 113, 119
Graul, H M 309
Gray, E L 460
Gray, J 31
Gray, J S 358
Gray, T 342
Grayson Smith, H 540
Greeley, H 104
Green, C 240
Green, H 466, 470
Green, H C 273
Green, H S 471
Green, J R 378
Green, J W 428
Green, R 225
Greenberg, S M 504
Greene, F A 280
Greene, Lord 389
Greenough, G B 436
Greenslade, R M 253
Greenstein, J P 238, 240, 387
Greenwood, A W 172, 176
Greenwood, H W 420
Greenwood, J A 170
Greenwood, J N 436
Greenwood, N N 338
Gregg, J R 315, 320
Gregg, S J 97
Gregory, B A 461
Gregory, F G 31
Greig, J Russell, 424
Gresson, R A R 135
Griess, P 120, 126
Gridgeman, N T 499, 501, 503
Griffith, R L 399
Griffiths, J H E 497
Grimley, T B 196
Grindley, J H 521, 525
Grison, P 312, 314
Griswold, J 46
Gröbner, W 34
Groth, P 578
Groth, W 267
Gruenz Jr, O O 272, 274
Grummer, M 164, 259
Grummitt, O 159, 283, 519
Grundmann, C 455, 461
Guckel, M 267
Gudmundsen, J G 508
Güntelberg, A. V 278
Guerrant, N B 499, 501, 503

Guest, H 383
Guggenheim, K 502, 504
Guilford, J P 355
Guillaume, Ch -Ed 152
Guinier, A J 399
Gulland, J M 240
Gump, W 145
Gurli, K 336
Gurney, R 202 207
Guterman, C E F 253
Gutfreund, H 442, 445, 447
Guthzeit, M 145
Gutmann, V 338
Gutstein, N 114, 119
Guyer, A 113
Guyot, O 145
Gyorgy, P 421, 424

Haak, F A 509
Haas, P 365
Haddow, A 31
Hadfield, D 82
Hadfield, R A 150
Hagg, G 229, 327
Hagglund, F 64, 67
Hagglund, S E 67
Hansel, G 22
Hagenguth, K 314
Haggard, H W 358
Hagstrum, H D 261, 267
Hahn, F L 555, 557
Hahn, O 375
Hahnel, E 119
Halmøy, E 508
Haldane, J B S 172, 356, 358
Hall, C L 364
Hall, N F B 126
Hall, W H 387
Halliday, I M D 309
Halsall, T G 183
Ham, J L 547
Hamburger, H 140, 145
Hamilton Whyte, W 327
Hammarsten, E 386
Hammett, L P 125, 127
Hammick, D L 127
Hammond, D H 249, 253
Hammond, J 31, 171, 173, 176
Hammond Jr, J 176
Hamner K C 252
Hanby, W E 513
Hanley, F 62
Hannah, M 285
Hansen, M 23
Hansford, R C 234
Hanson, D 436
Hansson, A 176
Hantzsch, A 122, 127
Happ, S C 560
Hapley, F 513
Hardwick, P J 374
Hargreaves, M E 399
Hariu, O H 165
Harker, D 8, 12
Harkins, W 532
Harkins, W D 336
Harland, S C 226, 373
Harper, A A 135
Harper, R 350, 355
Harries, C 145
Harrington, T M 458, 461
Harris, E J 364
Harris, G H 378
Harris, M 513
Harris, R J C 31
Harris, R V 252
Harris, S A 421, 424
Harrison, G R 372
Harrison, R W 120
Harrison, V G W 470
Harrod, R F 183
Harteck, P 267
Hartley, A C 226
Hartley, G S 185, 456, 461
Hartley, Sir Harold 31
Hartley, K 265, 267
Hartmann, J 73
Hartree, W 364
Hartridge, H 181
Hartshorn, L 371
Harvey, W 276, 486
Hasselbach, B 513
Hasse, H 34
Hassell, O 52, 484, 504, 507, 509
Hastings A B 320
Hastruid, A 547
Haszeldine, R N 431
Hatch, F H 184
Hatschek, E 259, 525
Hatta, S 110, 113
Hatton, R G 250, 252
Hauge, S M 503
Haughton, J L 280
Hauser, C R 159
Hauser E A 86, 90
Hausmann, L 336
Hautot, A 96, 196
Havinga, E 382
Hawkins, E G E 461
Haworth, E 460
Haworth, Sir Norman 50, 142, 145, 428
Haworth, R D 63, 67
Hayek, E 126
Hayes, J R 552, 557
Hayes, K A 171
Hayman, H W 83
Hazel, L N 173, 176
Hearman, J 251, 253
Heden, S 67
Hediger, H 471
Hedin, R 74
Hedvall, J A 73
Heer, C V 538, 540
Heertjes, P M 254, 259, 286
Heidelberger, C 229
Heidenreich, F 539
Heilbron, Sir Ian 181, 186, 280, 453, 457, 459, 461
Heisenberg, W 200, 540, 567
Heisig, G B 557
Helfenstrein, A 461
Hench, P S 423
Henderson, Y 358
Hendrick, C 461
Hendricks, S B 399, 504, 508
Hendry, A W 303, 328
Henglein, F A 23
Henisch, H K 519
Henriques, V 358
Henry, H 114, 119
Henry, W 85
Heppel, H K 531
Herasymenko, P 23
Herbst, W A 163, 165
Herdan, G 35, 41, 386, 447
Herington, E F G 41, 46, 289, 582
Hérissey, H 63, 67
Hermans, P H 257, 259
Hershberg E B 192
Hershey, R L 255, 259
Herthorn, J 462, 465
Hertz, H R 72
Herzberg, G 261, 264, 267
Hesser, C M 357, 359
Hetland, E 52
Hewitt, E J 59, 62
Heymans, C 355, 358
Heymans J F 356, 358
Heyne, W 337
Heyrovsky, J 19, 22 374
Heywood, H 259
Heywood, R B 299, 303
Heyworth, Sir Geoffrey 280
Hibbert, H 63
Hickman, K C D 547
Hickson, V M 328
Hickson, V N 302
Hill, A G 497
Hill, A V 364
Hill, R A W 569
Hillebrand, W F 74
Hillier, J 519
Hills, N G 125, 127
Himmel, J P 549
Hinckley, J W 255, 259
Hinde, R M 399
Hindle, E 31
Hinman, W S 347, 350
Hinsberg, S 73
Hinshelwood, Sir Cyril 31, 126, 193, 576
Hipple, J A 519
Hirschberger, J 145
Hirschlaff, E 540
Hirst, M 510, 513
Hirst, W 337, 433
Hixson, A W 109, 113, 259
Hoar T P 484
Hoare, C A 180
Hoberman, H D 383
Hoblyn, T N 253
Hoch, H 503
Hoch, R 503
Hodge, A J 364
Hodge, H C 461
Hodgkin, A L 364
Hodgson, H H 155, 159, 186, 188, 580
Hodgson, R E 176
Hölder, O 41
Hoerr, N L 319
Hoffmann, R 259
Hofreiter, N 34
Hofrichter, C H 462, 465
Hoftijzer, P J 109, 113
Hogness, T R 267
Hohenstein, W P 374
Hohn, H 16, 22, 407, 417
Holdam, J V 170

Holden, A N 493, 495, 497
Hollaender, A 387
Holler, A C 580
Holliday, A K 196
Holloway, F A L 109, 113
Holman, W I M 225
Holmberg, B 63, 67
Holmes, E L 447, 452
Holmes, H N 580
Holmes, H P 547
Holness, H 557
Holt, P A 163, 165
Holter, H 274, 276, 315, 319, 327
Honda, K 342
Honig, P 259
Honsberg, W 410
Hooke, R 249
Hooker, D R 358
Hopff, P P 504
Hopwood, W 528
Horn, M J 513
Horton-Smith, C 31
Hoselitz, K 77, 82
Hotop, W 23
Houdremont, L 150
Hougen, O A 46, 108, 113
Houghton, H G 527
Houston, W V 536, 539
Howarth, L 180
Howe, R M 289
Howell, H G 262, 267
Howells, F R 49
Howes, F N 127, 131
Howes, R S 309
Howie, J W 225
Howie, J W 304, 307, 309
Hsu, J 359
Hsu, S K 461
Hubbard, R O H 46
Huber, W 461
Hüttig, G F 258
Hugel, C 327
Huggill, A W D 428
Huggins, M L 509, 513
Hughes, A 568
Hughes, E D 193, 243
Hughes E W 7, 9, 12
Hughes, J S 503
Hughes, R H 491, 497
Hughes, T P 237
Hughes, V 84
Hughes, W H 31
Hughet, J H 46
Hull, L W 547
Hume, E M 503
Hume-Rothery, W 280
Hund, F 267
Hunneman, R D 255, 259
Hunter, R F 453, 456, 461
Hunter, R G 540
Hurd, R M 549
Huse, G 12
Hutchings, L E 113
Hutchinson, W K 280
Huxley, A F 365
Huxley, T H 486
Huzita, A 503

Iball, J 580
Ilkovitch, D 23
Illingworth, W S 127
Inagaki, T 289
Ingersoll, L R 340
Ingold, C K 127, 193, 243, 455, 461
Ingold, C T 426
Ingram, D J E 497
Irish, P R 309
Irwin, J O 504
Ishikawa, S 457, 461
Isler, O 453, 457, 461
Ivens, G W 190
Ives, D J G 452

Jacks, G V 547, 550
Jackson, I C 540
Jackson, W W 48
Jacob, W 465
Jacobs, R B 547
Jacobs, S E 180
Jacobsen, C F 278, 320, 513
Jacobsen, J C 274
Jacobsen, O 278
Jaeckel, R 543, 547
Jaffe, M 553, 557
Jakes, M 581
Jakob, M 259
Jakus M A 364
James, H M 171
James, R W 399
Jander, G 338
Jane, R S 525
Jeanloz R 428
Jedrzewski, N 267
Jeffrey, G H 148, 191
Jellinek, K 136
Jen, C K 496
Jenkins, F A 266
Jennings, J 426, 465
Jenny, L 196
Jenrette, W V 238, 240
Jensen, C 503
Jensen, P K 279
Jessop, H 303
Jessop, R S 267
Jeunehomme, W 267
Jewett, E E 258
Jönsson, O 73
Johansen, A 278
Johansen, G 278
John, J L 59, 62
Johnson, A L 309
Johnson, A W 461
Johnson, F B 235
Johnson, P 525
Johnson, R C 375
Johnson, R L 383
Johnson, R M 502, 504
Johnson, W 463, 465
Johnston, C 461
Johnston, T Y 584
Johnstone, A F 113
Jones, D B 513
Jones, E 183
Jones, E R H 147, 180, 461
Jones, F L 528
Jones, F W 399
Jones, G 90
Jones, H 196
Jones, J 370
Jones, J E 196
Jones, L A 96
Jones, P L 226
Jones, R C 399
Jones, R N 192
Jones, R V 99
Jones, Sir Walter Benton 280
Jones, W E 461
Jones, W G M 50, 145
Jongen, G H 500, 503
Jordan, D O 34, 139, 240
Jordan, P S 176
Jorgensen, C A 253
Jost, W 208, 212
Jucker, E 461
Jullander, I 37, 40
Jung, C 392
Justi, E 138

Kabanow B 237
Kalinin, M 462, 465
Kamayama, N 343
Kamenetzky, F 209, 212
Kamerlingh Onnes, H 534, 540
Kanganskaya, K Ya 337
Kann, S 499, 503
Kapff, S F 547
Kapp, R O 83
Kapulitzas, H 557
Karges, R A 338
Karrer, P 455, 457, 460
Karsten O 528
Kasch, J L 46
Kasper, J S 8, 12
Katz, B 359, 364
Katz, D 355
Katz, D L 257, 259
Katz J J 85, 470
Katz S M 97
Kaufman, M 244
Kaye, G W C 46
Kelley, T C 540
Keen, C D 349
Keesom, W H 537, 539
Kekcheyev, K 352, 355
Kekwick, R A 445, 447
Kellas, A M 358
Keller, W D 309
Kelley, E G 500, 503
Kellogg, C E 176
Kelly, H C 344
Kelly, K K 546
Kelly, L L 549
Kelvin, Lord 139
Kemmerer, A R 504
Kempf, R 553, 557
Kempthorne, O 215, 217
Kendall, E C 423
Kendall, M G 40
Kennaway, E L 358
Kennedy, J W 473
Kenner, J 124, 126
Kent, A J 355
Kent, C V 339
Kent, P W 427
Kent, W H 145
Kent-Jones, D W 280
Kepler, J 389
Kerby, L M 31
Keresztesy, J C 424
Kersta, L G 274

Kersten, M 78, 82
Kesel, R G 27
Kestelman, H 31
Keyes, D B 41, 46
Keynes, R D 364
Khotinsky, E 465
Khym, J X 452
Kieffer, R 23
Kimball, A C 387
King, E J 330
King, F H 259
King, G 463, 465
King, M L 252
Kini, K A 584
Kinnear, N B 326
Kinoshita, M 540
Kirby, P L 578
Kirchhoff, G R 85
Kirk, R E 328
Kiser, O M 176
Kisliuk, P 496
Kistiakowsky, G B 262, 264, 267
Kitchener, J A 452
Kitt, G P 450, 452
Kjeldahl, J 275
Klason, P 63
Klein, W 240
Klemenc, A 126
Knipping, P 6
Knorr, L 465
Knudsen, M 185
Knutson J W 27
Koch, H 320
Koch, H A 113, 164
Koch, H P 146
Koch, K R 235, 237
Koch, W 502, 504
Kochendörfer, A 399
Koehn, R C 499, 503
Kölbe, H 182
Koenig, W 270, 274
Kofler, M 461
Kohlschütter, V 555
Kohn, H 267
Kok, J A 537, 540
Kolb, O K 282
Kolbuszewski, J 478, 483
Kolthoff, I M 473, 519, 557
Kolthoff, J H 22
Kon, S K 498, 503
Konig, E 253
Koniuszy, F R 422, 424
Konrad, E 463, 465
Konstantinowa-Schlezinger, M A 553, 557
Kopp, G A 273
Koppe, H 540
Kordes, H 253
Koren Lund, L 508
Korff, S A 350
Korotkyi, B 145
Koshi, W A 497
Kosten, C W 281, 407
Koster, J 416
Kowalke, O. L 108, 113
Kozeny, J 165, 257, 259, 386
Kraemer, E D 40
Kraemer, F O 97
Krafft, F 547
Kraitzer, I 465
Krakenberger, R. M 461
Krall, F 417
Krall, H 121, 126, 280
Kramers, W J 547
Kraner, H M 304, 309
Kraus, C A 125, 127, 339
Kraus, R F 456, 461
Krauze, M V 461
Kravkov, S V 355
Krebs, H A 503
Krehl, W A 502, 504
Kreilsheimer, K 350
Kressman, T R E 452
Krinbill Jr, C A 309
Krishna Murthy, S N 50
Kröger, C 209, 212
Krogh, A 364
Kroll, W J 547
Kronig, R 567
Krouchkoll, M 235, 237
Krugelis, E J 279, 318, 320
Krummenerl, T 196
Krythe, J M 50
Kuffler, S W 364
Kuhl, W 567
Kuhn, R 424, 454, 437, 461
Kuhn, W 138
Kulash, W M 314
Kullgren, C 65
Kulkarni, S B 52
Kulkarni Jatkar, S K 52
Kunitz, M 119, 240
Kupalov, P S 364
Kurtenaecker, A 557
Kuss, E 410
Kuzmenko, A A 338
Kwauk, M 161, 163, 165
Kyhl, R L 497
Kynch, C J 267

La Cour, L 119
Laby, T H 46
Lackman, D B 387
Lackmann, F H 503
Lacombe, P 436
Lacotte, C 314
Lacy, L Y 274
Laland, S 387
Lamarck, J B P 486
Lamb, Sir Horace 139
Lamb, W F 490, 497
Lamm, O 41, 444
Lamont, H R L 492, 497
Lampitt, L. H 34
Lancaster, J K 337
Land, E H 420
Landau, L 207, 399, 539
Landsberg, P T 567
Langdon, W M 41, 46
Lange, E 23
Lange, E G 314
Lange, P 63, 67
Langevin, M P 68
Langmuir, I 577
Langweiler, H 100
Lankelma, H P. 159
Lansing, W D 40
Lantzing, J C 461
Lanz, H 278, 320
Lapham, E G 347, 350
Lapworth, A 154
Laqueur, E 358
Larian, M G 259
Larke, L W 436
Lasarew, B 540
Lauer, H 171
Laurence, C H 126
Laurmann, E 538, 540
Lautsen, O 279
Lautsch, W 65
Laves, F 399
Lavoisier, A L 149
Lawrence, A S C 31, 525
Lawrence, E O 528
Lawson, A W 531
Lawson, J 339
Lazarides, T O 417
Lea, F M 259, 386
Leake, C D 421
Le Bel, J A 9
Le Chatelier, H L 149, 569, 576
Le Gallic, P 502, 504
Le Rosen, A L 461, 500, 503
Lederer, E 461
Lee, H 98
Lee, L 309
Lee, S B 383
Lee, W A 387
Leedy, H A 27
Lees, C H 576
Lees, G M 327
Legge, J W 329
Leggett, D M A 279
Lehany, F J 83
Lehmann-Echternacht, H 240
Leibnitz, G 486
Leicester, J 148, 191
Leighton, A E 280
Lemberg, R 329
Léonis, J 278
Leopold, B 67
Lepeschkin, W W 73
Lepkovski, S 424
Lesar, A R 309
Lesniuk, R 171
Leupold, U 315, 320
Leva, M 161, 164, 257, 259
Levan, A 50
Levene, P A 145
Levi, H 279
Levy, H 41
Lewis, B 100, 569, 576
Lewis, F M 244
Lewis, H 525
Lewis, W C M 136
Lewis, W K 161, 164, 257, 259
Lichstein, H C 120
Liebens, M 96
Liebhavsky, H A 557
Lifschitz, I M 399
Lighthill, M J 135, 327
Liljestrand, G 358
Linacre, E 429
Lindahl, P E 279, 316, 320
Lindberg, J 513
Linderstrøm-Lang, K 240, 275, 278, 315, 319, 513
Lindgren, B 66
Lindhard, J 365
Lindley, H 509, 511, 513

Lindström, B 320
Lindstrom, E S 382
Ling, G 365
Lingane, J J 22
Linnell, W H 280
Linnemann, E 120, 126
Linsey, R A 46
Linstead, R P 31, 280
Lipson, H 12, 394, 398
Lister, B A J 452
Little, R W 503
Littleton Jr J T 340
Livingston, R 496
Locher, L 326
Lockspeiser, Sir Ben 326
Lodati, D 336
Lodi, M 498, 503
Loeb, L B 528
Loening, E E 196
Loevenstein, H 408, 417
Loewi, O 421, 424
London, F 538, 540, 567
London, H 538, 540, 567
Long, E 193
Long, J D 548, 550
Long, L H 263, 267, 291
Longsworth, L G 447
Longuet-Higgins, H C 155, 159, 579
Lonsdale, K 9, 11, 83, 399, 441
Loomis, A L 68
Lopez, J A 503
Lorente de Nó, R 364
Loring, H S 238, 240
Lou, C H 365
Loubser, J H N 497
Loudon, J D 584
Louvois, F M 151
Løvtrup, S 278, 317, 320
Lowde R. D 579
Lowe, H G 196
Lowman, A 503
Lowry, O H 317, 320, 503
Lu, Pao-Chung 291
Lucas, K 365
Ludwick, T M 220
Lui-Sheng, T 267
Lukes, R 145
Lulla, B S 291, 582
Lunde, K 484, 509
Lundell, G E F 74
Lush, J L 172, 176
Lynam, T R 307, 309
Lynch, G Roche 280
Lyons, L E 147
Lyot, B 177, 180
Lysenko, T D 253
Lysholm, T 442
Lythgoe, B 299

Ma, S Y 145
Mabille, P 392
McAdams, W H 259, 429
McAfee, K B 497
McAlister, D 41
Macallum, H D 144
McArthur, I 511, 513
Macassey, Sir Lynden 370
McBain, J W. 283
McBride, G T 165
McCaig, M 82
McCann, D C 456, 461
McCarter, R J 164
McCarthy, E F 225
McCarty, M 240
McClendon, J F 27
McClure, F J 27
McCollum, E V 577
McCormick, N R 528
McCune, L K 164
Macdougall, D P 336
Macdougall, G 468, 470
McDougall, E I 225
McDowell, C A 267
MacEwan, D M C 397, 399
MacGillavry, C H 399
MacInnes, D A 447
Mack, H G 557
Mack, J E 496
McKay, F A 27
McKee, J H 547
Mackenzie, B F 145
Mackenzie, J 307, 309
McLennan, J C 540
McLeod, C M 119
McLeod, J H 540
McLintock, W F P 280
McMillen, E L 259
MacNichol, E F 84
Macrae, D 170
MacTaggart, E F 547
McTaggart, K 465
MacWalter, R J 461
Maddams, W F 192
Maddock, A G 473
Madison, T C 497
Mail, G A 314
Major, R T 421, 424
Majumdar, B N 461
Makkus, W 314
Malewski, A M 241
Malignani, A 541, 547
Maillard, L 569, 576
Mallmann, W M 120
Malloch, J G 559, 562
Malpress, F H 176
Malus, D F J 176
Manegold, E 259
Manley, R O B 131
Mann, T B 500, 503
Manikaja, S 67
Marboe, E C 72
March, F 145
Marcus, P M 540
Maréchal, A 176
Marechal, R 359
Mark, H 374
Markham, J J 207
Markoff, A 41
Marquet, M 178
Marrian, G F 31
Marsden, A W 83
Marshall, A L 267
Marshall, F H A 171, 176
Marshall, H 553, 557
Marshall, S 120
Martin, A J P 180, 510, 513, 537
Martin, D C 227
Martin, G 159, 165
Martin, W S 549
Marton, L 432
Martyn, D F 180
Mason, E A. 164
Mason, I L 171
Massart, L 217, 221
Massey, H S W 31, 279
Masson, J I O 326
Mather, K 34, 228, 565
Mathes, R C 274
Matheson, G L 163, 165
Matheson, J L 181
Mathews, O R 550
Mathews, S 86, 225
Matson, L E 171
Matsuura, T 457, 461
Mattson, F H 499, 503
Mauguin, C 48
Maule, J P 175
Maxwell, the Hon D C 370
Maxwell, E 540
Maxwell, J C 99
May, E 371
Mayer, J 502, 504
Mayné, R 314
Mayo, F R 244
Mays, J M 497
Meara, M L 330
Meek, J M 528
Meerwein, H 464
Megaw, H D 398
Megson, N J L 374
Mehl, J W 386, 461, 499, 503
Mehner, L 259
Meinke, W W 504
Meissner, W 534, 539
Meister, M 67
Melander, B 52
Melander, L 193
Mellan, I 530
Mellanby, J 358
Mellanby, Lady M 27
Mellen, G L 542, 547
Mellon, B G 85
Melnick D 503
Melville, H W 387
Mendel, J G 229
Mendel, K 248, 253
Mendelssohn, K 537, 539
Menschutkin, N A 126
Menter, J W 382
Mercator, G 198
Mercer, E H 510, 513
Merck, E 420, 583
Merck, G 420
Mérino, J 399
Merrington, A C 527
Merritt, F R 493, 495, 497
Merton, Sir Thomas 31, 82
Meserve, E R 461
Meshovsky, A 539
Messmer, G 303
Messner, G 409
Meunier, P 499, 503
Meyer, K 119
Meyer, K H 513
Meyer, S 473
Meyer, V 120, 126
Michael, W 473
Michalowski, S S 46
Michurin, L V 253

Mickley, H S 164
Middendorf, J A 50
Middlebrook, W R 512
Middleton, H E 549
Miescher-Rusch, F 356, 358
Milas, N A 453, 358, 461
Millar, A R 472
Millar, R W 41, 46
Millen, D J 193
Miller, A P 309
Miller, B F 120
Miller, C J 147
Miller, D 134
Miller, D C 268, 274
Miller, G L 509, 513
Miller, M A 90
Milner, M E 248, 253
Milne, J 342
Mindlin, R D 303
Miranda, L I 557
Mirsky, A E 238, 240, 386
Misani, F 240
Misener, A D 540
Mitchell, J W 196
Mitchell, P D 120
Mitchell, R I 225
Mitchener, A V 314
Mitra, K K 50
Miyagi, S 289
Möhlau, A 556
Molstad, M C 165
Moltchanoff, G 348
Montgomery H B S 251, 253
Montillon, G H 259
Montonna, R E 258
Moore, H 283
Moore, L A 500, 503
Moore, M H 253
Moore, P J 365
Moore, F 504
Morand, M 196
Morgan, E 135
Morgan, F 433
Morgan, R S 461
Morgan, W T J 119
Morgareidge, K 502, 504
Mori, T 145
Morrice, F 225
Morris, C J O R 457, 461
Morrison, A I 461
Morrison, F W 259
Morrow, R M 382
Morse, R D 163, 165
Morse, R S 547
Morton, F 280
Morton, R A 147, 180, 460, 503
Moses, M J 315, 319
Moss, C 417
Mossart L 120
Mott, N F 196, 202, 207, 519
Moyer, W W 144
Mozingo, R 422, 424
Mudd, S 547
Muller, G E 352, 355
Muller, H 98
Muller, K 314
Müller, P B 503
Muller, R 22
Muhr, G 159
Mulcahy, M 212

Mulder, G J 140, 145
Mulliken, R S 267
Munroe, C E 336
Murawkin, H 577
Murdock, C C 399
Murphree, E V 327
Murphy, A J 31, 226
Murray, H D 420
Murray, M M 27, 225
Murthy, S N Krishna 50
Muratti, I 98
Muskat, M 433
Myers, D M 83
Myers, J E 326
Myers, R J 283
Mylonas, C 303
Mynall, D J 171
Myrback, K 319

Nachod, F C 452
Næshagen, E 52
Naslund, M 320
Naftalin, J M 225
Naish, W A 135
Naniev, N P 193
Napier, S E 212
Narath A 478
Narod, M 503
Nash, T 212
Nason, H K 473
Nair, H 225
Nasri, L 503
Nastuk, W I 365
Nattrass, R M 253
Neal, R H 503
Needham, J 320, 487
Néel, L 79, 82
Neff, H 388
Nekrassow, N 237
Nelson, C N 96
Nelson, G H 259
Nernst, W 136
Neth, W 259
Nette, M 258
Neubauer, H 336
Neumann, E 336
Neumann, M 336
Neumann, R 547
Neurath, H 532
Neustadt, M H 553, 557
Newitt, D M 280
Newth, F H 51
Newton, Sir Isaac 389, 391, 486
Newton, L O 280
Newton, W C F 119
Nichols, J B 442
Nichols, M L 548, 550
Nichols, N B 171
Nielsen, M 356 358
Nielsen, N 279
Nier, A O 547
Nieuwenkamp, W 399
Nikuradse, J 525
Nisbet, H B 327
Nishina, Y 342
Nissan, A H 525
Nixon, I S 520
Noakes, G R 425
Norinder H 528
Norman, N 509

Norman-Jensen, B 320
Norrish, R G W 263, 267, 292
Norton, F H 309
Norton, F J 267
Norwine, A C 274
Nowicki, D H 547
Nowinski, W W 228
Noyes, A W 126
Nurse, R W 259, 386
Nutting, J 81

Oberhauser, F 553, 557
Obreimov, J W 235
O'Callaghan, J A 287
Ochsenfeld, R 534, 539
Ockrent, C 468, 470
Ockerse, T 27
O'Dea, W T 33
Odell, J H 259
Odell, N E 135
O'Dwyer, J J 207
Oehlenschlager, V 279
Oesper, R E 557
Oeijer, G V 547
Offner, F 365
Ogburn, S C 552, 557
Ogston, A G 445, 447
Olcott, H S 456, 461
Oldfield, R C 352, 355
Oldroyd, J G 244
Olin, H L 259
Oliphant, M L 180, 183
Oliver, D A 82
Olland, H 347
Olney, M J 194
Olofsson, B 511, 513
Olsen, C 276
Oncley, J L 442, 447
O'Neal, A M 549
O'Neill, H 226
Onnes, H Kamerlingh 534, 540
Orchin, M 192
Ordal E J 120
Ordtex, G S 130
Ore, S 508
Orent-Keiles, E 577
Oriel, J A 280
Ormel, H 314
Orning, A A 165, 257, 259
Orowan, E 397, 399
Orr, Lord Boyd 375
Osborne, E T 280
Oser, B L 499, 503
Osmond, F 150
Ost, H 142, 145
Ostwald, W 196, 524
O'Sullivan, D G 461
Othmer, D F 328
Ottar, B 508
Ottesen, M 278
Oudway, G L 240
Oughton, C D 420
Overbeck, C J 268
Overend, W G 238, 240, 387
Overton, E 365
Oyaert, W 221

Pack, D C 331
Pacsu, E 428
Padre, M 503

Palin, D E 11
Pande, A 73
Paneth, F A 473
Pannell, J R 520, 525
Pao-Chung Lu, 291
Parent, J D 163, 165
Parker, H H 147
Parker, J S 280
Parker, R M 547
Parrish, D B 503
Partington, J R 42, 136, 182
Partridge, M A 34 139
Partridge, S M 448, 452
Pascal, B 198, 326
Pascoe, K J 398
Pashley, D W 196
Pathasarthy, S 73
Patterson, A L 399
Patterson, E K 315, 320
Patterson, W L 513
Paul, H 255, 259
Paul, W 99
Pauling, L C 12, 48, 147, 267, 291, 461, 494, 497
Pavlov, I P 488
Payman, W 336
Peacocke, A R 387
Pearsall, W H 31
Pearson, J 135
Pearson, K 171
Pease, M 174, 176
Pease, R N 267
Pedersen, K O 442, 444, 447
Peel, E A 326
Peeters, G 217, 221
Peierls, R L 539
Pekar, S 204, 207
Pellett, F C 130
Pelzer, H 207
Penciolelli, G 177
Penketh, D D 498, 503
Penn, F I 547
Penney, W G 261, 263, 267
Penrose, R P 493, 496
Peppard, D 463, 465
Pérez, J J 532
Permin, P M 279
Perrin, J 442
Perry, J 342
Perry, J W 566
Pertusi, C 552 557
Perucca, E 85
Perutz, M F 11, 447
Peterhans, E 113
Petersen, W E 217, 219, 221
Peterson, G E 274
Peterson, J B 549
Peterson, W D 159
Peterson, W E 176
Pethica, B A 383
Pettersson, T 66
Pfeiffer, P 552, 557
Pfestorf, G 340
Pfister, X 113
Pfluger, E F W 355, 358
Pfriem, H 99
Phelps, E F 339
Philip, A R 309
Phillips, D C 49, 388, 579
Philips, H 511, 513
Phillips, H W L 280
Phillips, J M 259
Phillips, P H 503
Phillips, R S 171
Phillips, R W 172, 174, 176
Phillipson, A F 225
Philpot, J St L 444, 447
Piazolo, G 65
Pick, H 196
Pickard J A 259
Pickels, E G 443
Pickford, R W 352, 355
Pierce, I G 240
Piercy N A V 83
Pierotti, G 41, 46
Pierif, H B 456, 461
Pietrusza, F W 339
Pietsch, L H E 32, 426, 472
Pinckard, J H 461
Piper, J 279
Pippard, A B 538, 540
Pirani, M 540, 547
Pirenne, M H 351, 355, 488, 564
Piria, R 120, 126
Pirie N W 31
Pi-Suner, A 357, 359
Plackett, R L 216
Plank, R 547
Ploetz, T 143, 145
Plotnikof, I G 253
Plumpton, B I 497
Pohl, R W 196
Pohlmann, R 70, 73
Poincaré, J H 391
Polanyi, M 267, 337, 392
Polgar, A 461
Pollchik, H 259
Pollchik, M 164
Pollett, W F O 483
Pollister, A W 238, 240, 315, 319, 386
Polstein, S 374
Polya, J B 461
Pool, M I 432
Pope, F G 147
Poppe, W 73
Porter, A 166
Porter, A W 90
Porter, C W 73
Porter, D J 259
Portevin, A M 150
Posnette, A F 16
Post, H 462, 465
Potter, R K 274
Poulter, S R C 470
Pound, F J 14
Pounder, C C 181
Powell A R 557
Powell, C F 547
Powell, H M 10
Powell, R W 109, 113
Powell, W J 212
Poynting, J H 244
Praetorius, E 279
Preece, I A 327
Prema Bai, M 50
Preston, G D 399
Preston, the Hon R M 136
Price, L S 126
Price, W C 188, 267
Priestley, J 390
Priestley, J G 358
Prim, E 503
Prime, H A 52
Pugh, F M 336
Pugh, W J 280
Pummerer, R 145
Pumphrey, R J 180
Punnett, R C 171

Quackenbush, F W 503
Quarrell, A G 280
Quenouille, M H 213, 563
Quivy D 359

Raacke, I D 557
Rabinowitch, F 85
Rachinger, W A 398
Rademakers A 540
Raine, T 280
Rakitin, Y V 190
Rakshit, J N 126
Ralston, A W 330
Ramberg, E G 137
Ramdohr, P 184
Ramser, C E 550
Randall, J I 399
Ranganathan, B 50
Rankama, K 330
Rao, C R 216
Rao, K S 97
Rao, S K Sreepathi 50
Rao S Srinivasa 582
Rapson, W S 12
Raschig F 552, 557
Rask-Nielsen, R 315, 320
Rauch, P 336
Raucourt, M 314
Raumann, G 520
Ray, B R 447
Ray, P C 126
Rayleigh, Lord 178, 404
Raynor, G V 31, 196, 280
Reche, K 547
Record, B R 445, 447
Reed, D W 433
Reed, L 554, 557
Reed, R I 193
Reed, W A 165
Rees, A L G 511, 513
Rees, W P 189
Rees, W W 331
Regener, E 349
Regoel, L 192
Reggiori, M A 98
Regniers, P 359
Rehbinder, P 237
Reid, A F 452
Reid, E 462, 465
Reid, J C 229
Reid, R S 225
Reilly, J 123, 127
Reineke, E P 176
Reiner, M 228, 244, 483
Resnick, W 164
Retherford, R C 490, 497
Revallier, L J 286, 288
Reynolds, H H 339
Reynolds, O 520, 523, 525
Reynolds, P 528

Rhodes, A 190
Ribaud, G M 280
Ribeiro O 501, 504
Rice, F I 503
Rice, F O 267
Rice, K K 267
Richards, M B 225
Richards, I L 399
Richardson, F G 527
Richardson, F D 135
Richardson, H O W 432
Richardson, R W 235, 461
Richtzenhain, H 67
Rickes, F L 422 444
Riddeli, G L 465
Riddle, R A 226
Rideal, E K 90, 212, 226
Rieke, C A 267
Riesmeier A H 552, 557
Riesz, R R 272, 274
Rigby, G R 307
Rigg, Sir Theodore 131
Riley, C V 313
Riley, H L 452
Ring, H 497
Ringel, S J 513
Rinkes, J J 145
Rischbeit, P 145
Rittenberg, D 383
Ritterhouse, G 550
Ritters, F 267
Rittner, E S 73
Riverdale Lord 136
Riviera, B A 557
Rivlin, R S 244
Roach, W A 253
Roads, F A 196
Robbins Jr, L V 235
Roberts, A L 309
Roberts, C 279
Roberts, E R 383
Roberts, G E 331
Roberts, H E 196
Roberts, W O 171
Roberts-Austen, Sir William 150
Robertson, A 37, 41, 174, 176
Robertson, A J 212
Robertson, J M 9, 12, 579
Robertson, N R 267
Robertson, R H S 23
Robertson, Sir Robert 336, 378
Robertson, W H A 226
Robinow, C F 115, 119
Robinson, A 373
Robinson, G W 560, 562
Robinson, R 127, 154, 159
Robinson, Sir Robert 31, 63
Roche Lynch, G 280
Rodewald, H 145
Rodriguez, J 567
Rogers, D 49, 388
Rogers, J S 259
Rogler, E 464
Rohn, W 541, 543, 545
Roholt, K 279
Roll, P M 240
Rommel, O 73
Ronbo, A 461
Rosenblum, E D 383
Rosenthal, J 355, 358

Rossi, B B 564
Rossini F D 267, 519
Rotblat, J 196
Rotherham, L 436
Roughton, F J W 329
Royer, L 48
Rozits, K 319
Rubin, I C 46
Ruegger, A 457, 461
Ruhemann, B 540
Ruhemann, M 540
Ruich W L 421, 424
Rumpell H 259
Runius, S 67
Ruppel, A E 274
Rushton, W A H 364
Rusinov, K 497
Russell B 183
Russell, B 200
Russell, F S 31
Russell, J C 549
Russell, R W 279
Russell Greig, J 424
Rutterholz, A 184
Rutgers, A J 537, 539
Ruth, B F 255, 257, 259
Rutherford, D P 85
Rutherford, Lord 562
Rygh, O 194, 577
Ryle, J A 225
Rzymkowski J 196

Sabine, P E 407
Sadana, J C 504
Saez, F A 228
Sah, P P T 145
Sahama, T G 330
Sahyun, M 509, 513
St Clair, H W 70, 73
Salah, M K 461
Salisbury, Sir Edward 31, 82
Salt, R W 314
Sampson, J B 433
Sandell, E B 473, 557
Sanders, J V 382
Sandoval, A 461
Sandwall, C G 50
Sanger, F 428, 513
Sarett, L H 423
Sarjant, R J 136
Sarton, G 391
Sarver, L A 557
Sastri, M V C 584
Saunder, D H 10, 12
Saunders, A G 280
Saunders, O A 280
Sauvenier, D 196
Savage, J P 499, 503
Say, T 310
Sayers, J 284, 371
Sayre, D 84
Schaeffer, H 365
Schaeffer, A 557
Schafer, P 314
Schaffert R M 420
Schafranik, J 122, 126
Schambyre, P 225
Schatz, A 424
Schaum, K 259
Schenk, H 98

Schick, E 461
Schiokalf, R 549
Schiff, L I 531
Schiller, P V 355
Schilov, E A 193
Schindler, R 330
Schlafli, L 34
Schmerling, L 159
Schmid, G 73
Schmid, H 122, 126, 159
Schmid J 73
Schmid, R 264, 267
Schmidt, C F 357, 359
Schmidt, G 240
Schmidt, J 278
Schmidt, W 408
Schmitt, F O 364
Schneider F E 196
Schneider F L 315, 319
Schnurmann, R 192
Schoeller, W R 556
Scholmerich, P 365
Schonbein, F 554, 557
Schoenborn, E M 41, 46
Scholes, G 386
Schomaker, V 12, 31, 147
Schott, L 272, 274
Schott, L O 274
Schottky, W 519, 531
Schoutissen, H A J 122, 127
Schroder, W A 461
Schubert, J 452
Schümann, M 122, 127
Schuette H A 142, 145
Schulman, J H 90, 567
Schultes, A P 73
Schultz, J 315, 320
Schumann, W O 84
Schumb, W C 73
Schwartz, A M 566
Schwartz, B H 240
Schwartz, M 314
Schwartz, S 316, 320
Schwarz, H W 547
Schweidler, E 473
Schweitzer, A 359
Scott, A D 461
Scott, C E 109, 113
Scott, L 268, 274
Scott, M B 503
Scott, R B 539
Scott, W R 358
Scott Blair, G W 227, 355
Scripture, E W 274
Seaborg, G T 473
Seidel, V 177, 180
Seitz, F 196, 207, 531
Sellke, K 314
Selwyn, E W H 94, 474, 478
Semmler, F W 140, 145
Sengupta, S A 225
Sensel, E E 159
Sentis, M H 90
Serallach, J A 90
Sergeenkoff, B 465
Serle, A 336
Sevag, M G 386
Sexton, E L 461
Sexton, W A 190
Shalit, H 374

Shalnikov, A 539
Shanes, J C 364
Shantz, E M 461, 499, 503
Sharbaugh, A H 497
Sharpe, A G 338
Shaw, J 319
Shaw, J C 217, 221
Shaw, M 119
Sheehan, W F 291
Sheehan Jr, W F 267
Shelton, S M 416
Shen, S-C 316, 320
Shenstone, A G 180, 267
Sherman, W C 461
Sherwood, T K 109, 113, 547
Shidei, T 267
Shiras, R N 41, 46
Shoemaker, D P 12
Shoenberg, D 538, 540
Shooter, K V 148, 385
Shoppee, C W 455, 461, 473
Shore, M S 422, 424
Shortt, H E 180
Shorugina, H 67
Shull, C G 399
Shulman, R G 496
Sickles, G M 119
Sidgwick, N V 265, 267
Siegel, W 259
Siemens, G 221
Sierk, C F 176
Signer, R 463, 465
Silber, R H 364
Silley, C E 31
Silvela, F 369
Silverman, A 289
Silverman, M 120
Simmons, J W 497
Simon, A 259
Simon, F E 31
Simpson, B W 225
Simpson, J H 207
Simunek, R 23
Singer, C 438
Singleton, J H 383
Sitton, B G 250, 253
Skaupy, F 139
Skelly, H 212
Skempton, A W 483
Skinner, H A 265, 267
Skottsberg, C J F 279
Skovsted, A 50, 279
Slater, J C 540
Slichter, C S 259
Slobodin, Ya M 461
Slocumb C H 424
Smiles, S 147
Smith, A G 497
Smith, C S 398
Smith, E M 436
Smith, F J 183
Smith, F W 73
Smith, G C 194
Smith, G F 193
Smith, H C 280
Smith, H Grayson, 546
Smith, J E 180
Smith, J L 31
Smith, K A 387
Smith, K M 491, 494
Smith, I 484
Smith, L A 309
Smith, L E 147
Smith, R H 145
Smith, R K 294
Smith, W 424
Smith, W R 159
Smith, W V 497
Smolens, J 387
Smreker, O 259
Sneddon, I N 135
Snedecor, G W 217
Sneider, P 461
Snell, C T 183
Snell, F D 183
Snyder, E B 309
Sobel, A E 498, 503
Sobotka, H 499, 503
Søeborg-Ohlsen, A 315, 320
Sollner, K 72
Sogani, C M 579
Sohns, F 67
Sokolov, A I 73
Sollner, K 98
Solmssen, U 461
Solomonov, N M 528
Sommer, L H 339
Sommerfeld, A 538, 540, 567
Sondheimer, E H 139
Sondheimer, F 461
Soodak, H 139
Soper, F G 193
Sørensen, S P L 275, 557
Sosman, R B 234
Souders, N 41, 46
Southwell, C A P 280
Southwell, Sir Richard 31
Speakman, J B 510 512
Speakman, J C 584
Spearman, C 355
Spedding, F H 452
Spencer, L G 190
Spengler, O 145
Sperry, D R 254, 259
Spice, J E 569, 576
Spinks A 461
Spitnik, P 374
Spitzer, R 503
Springall H D 135, 260, 267
Sproule, D O 73
Squire, C F 536, 539
Sreenivasan, A 500, 503
Sreepathi Rao, S K 50
Srinivasa Rao, S 582
Stacey, M 114, 119, 145, 180, 239, 387, 428
Stackhouse, E 113
Stampfli, R 365
Stair, R 350
Stakman, E C 105
Stanier, Sir William 31
Stanton, T E 520, 525
Stapledon, Sir George 58
Starr, I 421, 424
Stasiw, O 196
Stather, F 513
Staub, H H 564
Stauffer, R A 545, 547
Staveley, L A K 569, 576
Steacie, E W R 263, 267
Stearn, A E 119
Stearn, E W 119
Stebbins, J 226
Stechele, F 140, 145
Steeman, J W M 288
Sternsburg V 176
Stein, G 386
Steinbach, H B 364
Steinberg, A 119
Steinberg, J C 269, 271, 274
Steiner, A 259
Steiner, C S 163, 165
Steiner K 540
Stella, G 359
Stern, R 503
Stevels, J M 282
Stevens, C M 547
Stevens, G W W 196
Stevens, J R 424
Stevens, S S 355
Stevens, T S 31
Stevenson, D P 263, 267
Stewart, F T 12
Stewart, G W 382
Stewart, Sir Halley 183
Stewart, H C 90
Stickley, E E 398
Stoker, W R 33
Stokes, A R 398
Stokes, G G 85
Stone, M A 212
Stoner, F C 80
Stoney, H H 27
Storch, H H 164
Storks, K H 382
Strain, H H 145, 283, 501, 504
Strain, H I 557
Strandberg, M W P 497
Straub, F 461
Straub, I B 339
Strecker, A 120, 126
Street, A 509, 513
Strickland, F H 314
Strijk, B 399
Strong, J 52
Stubbs, A I 147, 461, 499, 503
Stull, D R 44
Stumpf, P K. 73
Stutzman, L F 113, 164
Subrahmanyan, V 291
Subramaniam, M K 50
Sully, A H 32, 280
Sulzbacher, K 191
Summerville, W A T 547
Sumner, L 461
Suter, H A 557
Sutton, D H 547
Sutton, H 280
Sutton, L E 180, 569
Sutton, O G 139
Svedberg, T 442, 444, 447
Sverdrup, H 226
Swallow, J C 547
Swett, W W 176
Swick, R W 504
Swikert, M A 383
Sykes, C 399
Synge, R L M 180, 225
Syrkin, Y K 34, 139
Szalay, A 73

Tabor, D 382, 433
Tabor, D J 148
Taft, R W 243
Tai, C T 196
Tainton, U C 413
Tamman, G 209, 212
Tanaka, K 382
Tåning, Å Vedel 327
Tansley, A G 82
Tardy, H I 301, 303
Tasiley, E 122, 127
Tasker, H S 226
Tartaldi, H 498, 503
Tate, J T 261, 267
Taton, R 138
Tauber, H 553, 557
Taylor, A 80
Taylor, A M 340
Taylor, B 387
Taylor, D 284
Taylor, E S 120
Taylor, G I 34, 90, 336
Taylor, H J 27
Taylor, H S 97, 283
Taylor, J 186
Taylor, J B 578
Taylor, R J 501, 504
Taylor, T I 450, 452
Taylor, T W J 122, 126
Taylor, W H 48
Teece, I G 119, 145
Tellegen, F 509
Teller, E 267, 399
Teltow, J 196
Tempel, R B 569
Templeman, W G 190
Terrell, L I 119
Terrien, J 179
Terzaghi, K 259
Teilow, K S 186, 188
Tett, H C 280
Teunissen, H P 141, 145
Thannhauser, S J 240
Thenard, A 314
Thewlis, J 27
Thiel, A 267
Thoday, D 135
Thomas, P H 148, 385
Thomas, R W 142, 145
Thomas, V G 497
Thomas, W J 226
Thompson, A 143, 145
Thompson, C R 503
Thompson, Sir D'Arcy 198, 327
Thompson, F C 226
Thompson, H W 188, 425
Thompson, J 431
Thompson, J O 41
Thompson, R H S 119
Thompson, S Y 498, 503
Thompson, T G 27
Thomson, A M 225
Thomson, Sir George 31
Thomson, G H 355
Thomson, W 225, 259
Thomson, Sir William 342
Thornton, H G 31
Thouless, R H 353, 355
Threlfall, C J 240
Thring, M W 280
Thygesen, J E 278
Tiemann, F 140, 145
Tilley, C E 83
Tiselius, A 450, 452
Tishler, M 423
Titterton, E W 180
Todd, A R 239
Török, C 557
Tolansky, S 48
Tolbert, B M 229
Tollens, B 145
Tolman, R C 447
Tompkins, E R 452
Torrey, H C 531
Tosic, J 225
Toshimasa, S 503
Townes, C H 493, 495, 497
Toxopeus, H J 250, 253
Toynbee, P 392
Trabert, W 527
Tracey, M V 90
Treloar, L R G 138
Trevelyan, G M 326
Tribe, D E 225
Tribe, F M 225
Trilling, C A 164
Trim, A R 90
Tronstad, I 340
Trouvelot, B 312, 314
Troyan, A V 190
Tswett, M 554, 557
Tucker, W B 86, 90
Tudor, G K 212
Tulasne, R 115, 119
Tumanskiy, S S 73
Turkevich, J 234
Turnbull, H W 201, 326
Turner, J S 226
Tustin, A 166, 247
Tyndall, A M 578
Tyndall, J 487

Ubbelohde, A R 57, 207, 212, 331, 376
Uhland, R F 550
Umbrett, W W 114, 119
Underwood, A J V 255, 259
Ungar, J 387
Updike, O L 41, 46
Upton, P B G 289, 582
Urban, F 259
Urban, F M 352, 355
Ure, S G M 255, 259
Urey, H C 450, 452
Uttley, A M 171
Uvarov, B P 180

Vaisala, V 346, 349
Vaidya, R M 500, 503
Valatin, J G 262, 267
Valentine, S 162, 165
van Artsdalen, E R 267
van Berg, C F 46
van de Haas, H 259
van de Kamp, J 423
van der Grinten, L 420
van Dorp, D A 453, 458, 461, 504
van Eekelen, M 501, 503
van Ekenstein, A 145
van Gils, J P M 255, 259
van Ginneken, P J H 259
van Hasselt, J F B 145
van Hooren, C J 109, 113
van Krevelen, D W 106, 109, 113
van Laer, P H 537, 539
van Nieuwenburg, C J 374
van Rossum, L 196
van Someren, E H S 83
van Veen, A G 461
van Vleck, J H 263, 267, 492, 497
van't Hoff, J H 9, 208
Vandenbelt, J M 147
Vanderdriessche, L 240, 278
Vedel Tåning, Å 327
Vendrely, R 115, 119
Verdcourt, B 470
Verhagen, D 503
Vernon, C A 193, 243
Vernon, M D 355
Vernon, W H J 145
Versey, H C 135
Versluys, J 259
Verzar, F 358
Vesely, V 581
Vick, F A 135, 519
Viervoll, H 508
Vieta, F 197
Villee, C A 316, 320
Vines, M F R 212
Vischer, E 240
Visscher, M B 217, 221
Vivian, J E 113
Voge, H H 263, 267
Vogel, A I 148, 183, 191, 431
Vogt, M 365
Volkert, M 279
Volta, A 486
von Baeyer, A 484
von Bertalanffy, L 282
von Carman, P, C 165
von Elbe, G 569, 576
von Euler, E 461
von Euler, H 122, 126, 239
von Euler, U S 358
von Grote, A 145
von Helmholtz, H L F 85
von Hevesy, G 473
von Laue, M 6, 390, 540
von Leibniz, G W 138
von Mises, R 41, 386
von Neumann, J 267
von Winning, L 314
Vowles, L E 225

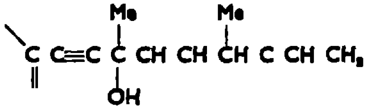
Waddington, C H 171, 228
Wagatsuma, S 349
Wagner, G H 119
Wagner, J 147
Wagner, R 355
Wain, R L 180
Waitz, K 235, 237
Waksman, S A 422, 424
Walde, H 22
Waldram, J M 33
Waldron, M B 196
Wales, M 41
Walker, W F 253
Walker, W H 259
Wall, M E 500, 503
Wallace, A R 487
Wallace, J M 252
Wallace, T 59
Wallach, O 120, 126

Waller, C 196
Waller, I 399
Walpole, G F 226
Walsh, A D 263, 267
Walshe, F M R 31
Waltcher, I 374
Walter, F 358
Walter, J F 113
Walton, H F 452
Wang Lund, E 508
Wanke, K 417
Wanner, H 315, 320
Ward, F R 580
Wardlaw, C W 83
Wardlaw, W 462, 465
Warren, B E 230, 235, 399
Warren, J W 267
Waterlow, J C 316, 320
Waterman, H I 254, 259
Waterman, R F 424
Waters, W A 155, 159, 193, 330
Watson, J 336
Watson K M 46, 108, 113
Way, W 465
Weaver, R 27
Webb, M 113, 119, 184, 240, 387
Webber, H C 255, 259
Weber, E H 353, 355
Weber, H 547
Weber, H H 364
Weedon, B C L 461
Wehmer, C 145
Wehrli, H 461
Weidenhagen, R 145
Weil, H G 547
Weiler, G 339
Weinberg, A 365
Weintraub, M 164, 259
Weiss, J 193, 386
Weissberger, A 34, 472
Weissenberg, K 483
Welcher, F J 557
Wellensieck, S J 50
Wells, A F 235
Wells, A K 184
Wells, M K 184
Welsch, M 114, 119
Welshimer, H J 115, 119
Wendt, G 424
Wenger, P E 374
Wenstrom, E 237
Wentinck, T 497
Werbin, H 498, 503
Werner, R C 46
Wertenstein, L 267
Wertyporoch, E 159
West, J 48
West, P W 552, 557
West, W 196
Westcott, C H 284
Westenbrink, H G K 278
Wettstein, A 461
Wexler, Aaron 534, 536, 539
Weyl, W A 72, 230, 234
Weyland, H 465
Wheeler, M A 436
Wheland, G W 156, 159
Whicher, O 326
Whipple, F L 31, 139
White, A 569
White, C E 553, 557
White, E G 225
White, H E 259
White, J U 264, 267
White, R G 171, 176
White, R R 41, 46, 164
Whitehead, A N 199, 326
Whiteley, A L 171
Whitfield, G W 470
Whitmer, C A 531
Whitmore, F C 159, 339
Whitmore, R A 500, 503
Whitney, R P 113
Whittaker, J M 83
Whyte, W Hamilton 327
Wicke, F 267
Wiener, N 489
Wiggins, L F 50, 140, 145, 239
Wiggle, A F 259
Wigglesworth V B 31
Wight Bakke, E 5
Wightman, P D 486
Wignall, I W 126
Wigner, E 267
Wilberforce, S 486
Wilchinsky, Z W 399
Wilhelm, J O 540
Wilhelm, R H 159, 161, 163, 165
Wilkes, J B 503
Wilkes, M V 139
Wilkinson, H 461
Willard, H H 555, 557
Williams, B R 135
Williams, D 279
Williams, E G 126
Williams, I C 84, 171, 180
Williams, G C 113, 528
Williams, J W 41, 52, 447
Williams, M C 540
Williams, N F 461
Williams, N H 492, 497
Williams, R J 421, 424
Williams, R R 421, 424
Williams, T I 374
Wills, J H 461
Wilms, G R 436
Wilson, A J C 49, 388, 394, 398, 579
Wilson, C G 578
Wilson, C L 461
Wilson, D C 27, 225
Wilson, D W 358
Wilson, E B 491, 497
Wilson, H F C 461
Wilson, J B 383
Wilson, K S 253
Wilson, M 225
Wilson, P W 382
Wilson, W J 193
Winand, L 196
Winder, C V 359
Winge, Ø 276, 279
Winkler, F 241
Winkler, H 252
Winslow, E H 557
Winter, E R S 383
Winter, G 465
Winter, N 179
Winternitz, W 499, 503
Winters, L M 176
Winterstein, H 356, 358
Wise, G H 503
Wistar, R 159
With T K 504
Withner, C L 253
Withrow, A P 252
Withrow, R B 252
Witte, M A 209
Witty, R W 542, 547
Witzmann, H 259
Wöhlisch, E 138
Wohl, K 41, 46
Wohlers, H 554, 557
Wohlfarth, E P 80
Wolf, D E 422, 424
Wolfrom, M L 428
Wood, R G 579
Wood, R W 68, 340, 580
Wood, T R 422, 424
Wood, W A 398, 436
Woodhead, D R 336
Woods, H J 511, 513
Woodward, P 212
Woodworth, R S 352, 355
Woolf, A A 338
Woolley, J M 428
Work, L T 259
Wormald, H 253
Worner, H K
Worthington, A M 86, 90
Wright, S 172, 176, 359
Wright, W D 285, 353, 355, 364
Wrisberg, Sir Frederick 370
Wunderly, C 532
Wyckoff, R W G 565
Wynne, W P 580

Yagoi, N 163, 165
Yankwich, P F 229
Yates, F 213, 215, 217
Yerkes, L A 547
Yoe, J H 519, 557
Yoffe, A 212
Youd, C S 330
Young, A C 365
Young, E G 281
Young, G 365
Young, J Z 135, 280, 282
Young, L 73
Young, L 235
Young, M Y 120
Yudkin, S 498, 503
Yukawa, H 341

Zachariasen W H 399
Zahn, H 512
Zamenhof, S 238, 240
Zappfe, C A 305, 309
Zavadovskii, B M 176
Zechmeister, L 461, 502, 504, 557
Zemplen, J 264, 267
Zeuthen, E 276, 279, 316, 318, 320
Zienau, S 207
Zittle, C A 239
Zocher, H 557
Zotterman, Y 358
Zscheile, F P 500, 503
Zsigmondy, R 97
Zucker, F J 326
Zuckerman, S 31
Zuhr H F 547
Zunker, F 259
Zwikker, C 281, 400, 487
Zworykin, V K 137

Corrections

Page	*Col*	*Line*	*The line should read*
39	L	7	$\mathcal{N}(x) = \Phi(x) = \frac{1}{2}[\theta(x) + 1] = \frac{1}{\pi^{\frac{1}{2}}}\int_0^x \exp(-x^2)dx + \frac{1}{2}$
66	R	—	Formula *XIV* should contain a double bond in the side chain There should be no double bond in formula *XV*
86	R	30	ϱ_2 are the densities of the two phases in gm/cm³,
88	R	5	medicinal paraffin drop was suspended in one
135	R	22	WILLIAMS (Economics), Dr F A VICK (Physics),
288	R	30	nitrogen dioxide and sulphur trioxide In mixtures with
288	R	34	trioxide and nitrogen dioxide
385	L	Eqn 1	$\frac{\lvert E(f/g) - E(f)/E(g) \rvert}{v_g^2} - K < \frac{\sigma_f}{\sigma_g}$
444	L	9	steel or duralumin
460	L	—	Formula *XXX* should read  $\underset{\Vert}{\diagdown C}\ C{\equiv}C\ \underset{OH}{\overset{Me}{C}}\ CH\ CH\ \overset{Me}{CH}\ C\ CH\ CH_3$
507	R	24	is not a naphthodioxane but bi-1,3-dioxa*cyclo*pentyl (2)

Commentary:
Research and Practice in Industrial Relations

ENGINEERS AND DOCTORS have long since accepted the most basic research efforts of the natural and biological scientists as highly practical. Managers and leaders of human organizations, of companies and unions, still are doubtful about the practical value of basic research in the field of human relations and organization. The psychological and social scientists cannot be sanguine about this matter for these men are the managers of essential 'laboratories' in which their research must be carried on and their hypotheses tested and corrected.

One of the major barriers to the confidence of practical men in the findings of psychological and social science, and indeed to the validity of the findings themselves, is the fact that the data examined are sought in situations considerably removed from those in which practical men must apply them. This is no criticism of the rat maze, the analyst's office, the clinic, the fatigue laboratory, the islands of the Pacific, and other research situations used by students of behaviour. It is simply a recognition of the fact that scientific hypotheses are not adequately formulated until based on generalizations from the observation and analysis of the precise facts they seek to explain. Derived from a study of other types of facts, they are suggestive of clues and of problems to be explored in research in the actual field of application. As such they are extremely fruitful. They do not, however, provide definitive principles for practice in that field. It is a long jump from the rat maze or the Hottentot society to the modern factory or union hall. These field 'laboratories' in companies and unions are in charge of the managers and leaders of those organizations. Hence a need for a partnership in research between these practical men on the one hand and the psychological and social scientists on the other, that each may understand the contribution of the other to the realization of his objectives, and that through their joint efforts they may produce in the area of human relations and organization a scientific guide to practice similar to that in possession of the technical engineer and the doctor.

This commentary is an attempt to lay the ground work for such a partnership first by indicating the relevance of theory to the improvement of practice, secondly by suggesting a framework for study of human relations in industry which gives both practical and scientific promise.

It is normal in any field of activity to consider a man practical if he has a knowledge of techniques and the skill to put his knowledge to work. There is, however, another candidate for the title 'practical man'. He is the one who knows not only *what* will work but *why* it works, the manager who knows the principles of human behaviour so that he can predict whether a technique of dealing with human beings, successful in London, will work in Bolton or Cardiff; the leader who can predict whether organizing methods successful among engineers in a privately owned textile mill in Lancaster will work in a publicly owned utility in Sheffield , the man, in other words, who knows enough about cause and effect laws in human relations so that he can develop sound long range strategy which keeps changing tactics 'on the beam'

Effective action can be guided by accurate and adequate theory I have long since ceased to be apologetic in urging the importance of theory to practical men They recognize the necessity for theory in their problems of technology, and they use theories of human behaviour in organizing and directing their employee and membership relations and their relations with each other Their theories are summaries of their conclusions from personal experience The question is not whether they will use theory, but whether the theory they do use is consistent with the facts and adequate to the tasks they face

An analogy from the field of medicine is pertinent At one time medical practitioners proceeded on the theory that ill health was caused by devils in the body In industrial relations we are still operating at times on a similar theory Later, making use of a prominent aspect of the human organism, doctors operated on the theory that the cause of ill health is rooted in the maldistribution of blood In industrial relations this is similar to our still most prominent theory that industrial unrest is rooted in the maldistribution of income

These medical theories did not make possible medical practice which could produce a satisfactory degree of individual or public health Lacking an adequate theory, what was done ? Reliance had to be placed on the unusually experienced, competent, sensitive, and wise individual who seemed intuitively to know the principles of good health Or it was placed on the successful users of traditional and folk remedies who knew *what* to do but not *why* they did it

In industrial relations we are doing the same thing Lacking an adequate theory of human relations on the basis of which to train leadership, we must count on the chance that we will be able to find a 'natural born leader' who is unusually wise and sensitive and intuitively right, or who has been a successful practitioner of folk remedies Such men have done a fine job But since their experiences are not clearly and systematically related to a theory of cause and effect in human relations, since they can tell us chiefly what to do and not why it is done, the secret of their success cannot be widely communicated and understood in situations in which important and crucial factors differ from those in which success has been achieved The elements of success cannot be analysed and generalized and be made the basis of training for men charged with the responsibilities of leadership, whether in industry or in unions

Now I would not disparage the attention to tactics in industrial relations today any more than I would disparage the study of tactics among the medical practitioners of the 18th century But I would like to point out that attention to tactics alone would never have resulted in the improvement in human health we enjoy in the 20th century Practitioners would have devoted their attention to the development of sharper and less pain producing needles, to the angle of incision, to the question of whether bleeding was most effective in the morning or the evening, under the influence of drugs, or not *etc* Progress in individual health and in public health programmes awaited the development of an adequate theory of anatomy and of 'physical' relations

I would suggest that theory is the most 'practical' thing in the world, and that progress in human relations and organization will owe a great deal to research which sets an adequate theory as its goal To be specific, research designed to answer the question, 'Why do men behave as they do ?' is needed to supplement the wisdom-of-experience of practical men

That view can be stated more specifically We need studies not only of personnel policies and practice, but of the nature of persons , not only of incentive systems, but of human incentives , not only of collective bargaining procedures, but of the factors that mould the attitude and actions of bargainers , not only of techniques for organizing enterprises or unions, but of the principles of effective association and group solidarity and teamwork Management and unions can jointly support such studies for they are designed to develop principles of human behaviour equally relevant to the tactics of both.

Such research is not an alternative to the lessons of experience of practical managers and union leaders. The function of all research in human relations is to collect and systematize experience. There is a sense in which research is a process for broadening experience so that the individual may have a wider range of facts and principles against which to check his own lessons of experience. But basic research goes beyond the collecting and systematizing of experience. From its findings an attempt is made to derive hypotheses about cause and effect relations and to test and perfect these hypotheses by systematic observation and experiment.

Let me say immediately that I have no hope that the organization of human relations can be reduced to an applied science. The variety of human needs and aspirations is so great, the circumstances surrounding the activity of any group so complex, that a science of human relations can be only an aid to vision, courage, common sense, artistry, faith, and other requirements for effective leadership , but it is an essential and indispensable aid in the exercise of those capabilities. To put it bluntly, vision is no substitute for understanding , courage is no substitute for intelligence , common sense (which is a mirror of common experience) is no substitute for systematic knowledge , artistry is no substitute for principles of action , faith is no substitute for science.

A FRAMEWORK FOR STUDY

If we are to make this partnership between the man of action and the scientist effective, we must have a framework for analysing problems of human relations which contributes to the purposes of both. If, when they think about those problems, they are using the same framework, not only will their observations and generalizations reinforce or correct each other, but they will be able to speak a common language. I would like to suggest in very elementary form a possible framework which could serve these ends.

The most important thing is that we agree on the nature and structure of the thing we are studying. When we study human relations in a company or union what fundamental picture do we have in our minds of that company or union ? One of the things that has kept our many observations from adding up to a set of usable principles is that we don't all have the same basic picture. To some a company is a production line, to others a big family, to others a crowd of difficult but promising individuals, to others a list of numbers on a payroll, to others a group of supervisors and employees. To some a union is a group of members, to others a revolutionary association, to others an insurance company, to others an army, to others a department of the enterprise *etc*. Because we start off with different pictures our observations have a different focus, and on completion our reports do not fit together so that general principles can be formulated.

Now when we attempt to analyse the health of the human relations in a company or a union what is going to be our picture of the nature and structure of the thing we are studying ? That picture will determine what we look for, how we analyse and organize our findings, and whether we report our investigation in a way which is practical in helping to maintain or improve the health of those human relations. Those of us at the Yale Labor and Management Center have come to a conclusion on that matter which guides our research. It is a conclusion which grows out of not only our training in social and psychological science, but also our studies of companies and unions and our practical experience as consultants and arbitrators. It is a conclusion we share with a number of our colleagues in other universities. I think it will coincide with the experience of men of action. It is very simple.

A company or a union is a small society, it is a social organism. As the body is a physical organism composed of cells which work together through the operation of certain organizational devices or systems, so the company or the union is a social organism composed of individual people who work together through the operation of certain organizational devices or systems. What are those systems in this social organism which bind the individuals together in a working team?

First is the *organizational charter*, the concept of the organization as a whole, its purposes, policies, significance, and reputation The organizational charter is reinforced by traditions, written statements and constitution, and the material and human symbols which make vivid and secure this concept of the organization as a whole in the minds of the members

The second is the system of *functional specifications* This is the definition of the functional roles to be performed by the several members individually and collectively with particular reference to their functional relationships with other members of the group

Third is the *status system*, which organizes the members into a hierarchy of authority and deference and defines the privileges and responsibilities relevant to authority and deference which go with every position in that system

Fourth is the *communication system*, by which the information required for effective working together is transmitted from one individual to another.

Fifth is the *reward and penalty system* by which individuals are persuaded or compelled to act in ways considered advantageous to the organization

There are other systems such as *technology* by which individuals are related to each other by reference to the tools with which and materials on which they work But these will do as illustrations

Our basic conception of a company or union as a society or social organism, then, suggests a systematic outline of the aspects of that society of which the efficiency of operation will be the object of our study, whether we are trying to improve our practice or whether we are trying to understand the principles of human behaviour, which takes place among the individuals organized as members of this 'society'.

That sounds elementary, doesn't it? Well, starting points and fundamentals are always elementary But unless we have a common conception and understanding of fundamentals we will be hopelessly lost when we begin to rear a more complex structure of principles and practice on that foundation Imagine how much of a contribution a group of doctors would make to a developing science of physical relations, one of whom considered the body to be an organism, another a machine, another a gaseous compound, another the battle-ground for devils and angels! A common agreement on the essential nature and structure of a company or union is essential for those who want their diagnoses and studies to add up, to be cumulative, to contribute to a developing science of human relations

Our next difficulty in making our observations add up to something is that we have not developed a uniform set of tests or standards by which we can appraise whether that society and its organizational devices are operating well or poorly, whether they are healthy or unhealthy

Where will we get our tests for the organizational charter, the functional specifications, the status, communication, and reward and penalty systems? I have one suggestion for a set of tests which I think will not only prove of practical utility for men of action, but which are essential for the purpose of building a science of human relations In general these tests pose the question, 'Do these organizational devices or systems help or hinder people to realize their goals, to achieve their standards of successful living?'

The reason for this type of test is clear The participants in a company or union are trying to live out a satisfying and successful life in the midst of that society They have certain goals or standards of satisfactory or successful living, many or most of which they share with the rest of the members, by which they measure their degree of achievement From the point of view of the members of an organization, that organization is healthy if it helps them to achieve those goals, and it is unhealthy if it frustrates them But do not think for a minute that such tests are of personal interest merely to individuals They are equally tests of the productive capacity of a company or the strength of a union.

So, as a second step I suggest that we set up a set of tests for them which will make us aware to what degree each of the systems satisfies the major goals people have

To the system of functional specifications we put a series of questions to test whether or not it helps the participants to achieve their goals of respect, creature comforts, control, understanding, capacity performance, integrity, security, progress and justice[*] These are the major goals that we have found present in our investigations of worker, management and union leader groups in England and the United States since 1932 We make no claim that they are complete or universal, or that they will not be substantially modified by additional research To the status system we put questions serving the same purpose, then to the communication and reward systems, the organizational charter, technology *etc*

Now with that conception of our problem and that systematic framework for study we are ready to begin I will not go into the problems of sampling and interview methods Those are research techniques But suppose we have gone ahead and completed our investigation and gathered our material and have it summarized Where do we stand

At this point we have a pretty good picture of the actual structure of human relations in the organization, and of the reaction of the participants to it Moreover, that structure being what it is, we can suggest why the reactions were favourable or unfavourable in terms of what goals were brought within reach or were out of reach

I just want to observe that, to this point, any manager or leader who wishes to make practical use of such findings will find that possible He can conclude, 'My production and turnover figures in Department A indicate that teamwork is at a low ebb This analysis suggests that the trouble focuses in the status and communication systems It also shows up in some detail why those systems are unsatisfactory from the point of view of the members of that department My problem is to see what I can do about modifying those organizational bonds so that those inadequacies will be removed'. The union leader facing poor teamwork in a local would be able to chart his course in the same way

In other words, from the point of view of the participating company or union there is no ivy growing on the results of such an investigation. It is a diagnosis which can be made the basis for immediate decision and action

Equally important, however, is that the scientist has at his disposal data from which he can derive hypotheses concerning the relations between how men are observed to act and the circumstances and motives from which that action springs His work has just begun He has before him materials from actual laboratories from which, by careful analysis, to derive principles of human behaviour and organization which can be tested in those same laboratories

The work of the social scientist has just begun He must now go to work on this material, compare observed results in one department with those in another He must explain observed differences in terms of the causes suggested by the data He draws up preliminary generalizations about cause and effect He studies the relation between what men were observed to do and what goals they had, and the way their social environment in the company or the union affected their achievement of those goals And all the time he keeps asking, 'Why did those people behave that way?' He sharpens his terms, he fills them with vivid content from actual life He corrects his basic conception of the structure and dynamics of human relations. He casts a critical eye on his methods Then he is ready to tackle the next investigation, take his generalizations and principles into the next company or union laboratory and put them to a further test So the process of building a science goes on

In this manner the man of action and the social scientist can go on together, partners in the development of immediate guides for improvement of teamwork in organizations and in the slower but equally important process of developing a science of human relations

E. WIGHT BAKKE

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[*] An explanation of their content will be found on pages 12ff of the Yale Labor and Management Center publication, *Adaptive Human Behavior*, and in two articles by the author 'Need for Scientific Study of Human Relations in Industry', *Advanced Management*, Vol XII, No 2, and 'Teamwork in Industry', *Scientific Monthly*, Vol LXVI, No 3 Reprints of the above articles may be obtained from the Yale Labor and Management Center, 333 Cedar St, New Haven, Conn

X-Ray Structure Analysis of Complex Organic Compounds

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THE analysis of the diffraction patterns produced when crystals are exposed to x-rays has led, in the last two decades, to a considerable increase in our knowledge of the structures of organic molecules Previous knowledge, based on logical inference from the empirical data of the organic chemist, from chemical analysis and from chemical synthesis was essentially non-quantitative in character, the new method, physical rather than chemical in its attack, has not only confirmed and extended this knowledge but has also yielded precise metrical information concerning molecular dimensions The present article will deal with some recent developments in the application of x-ray analysis to complex organic compounds, in order to do this, it will first be necessary to review the general background of x-ray crystallography

The study of molecular architecture by means of x-ray diffraction became possible in 1912, when M VON LAUE first suggested that the regularly spaced arrays of atoms which constitute crystals might act as a three dimensional diffraction grating for x-rays This suggestion was acted upon and confirmed by W FRIEDRICH and P KNIPPING, and in the following year W H and W L BRAGG were already able to determine the structures of some simple crystals, sodium chloride, potassium chloride, and diamond Symmetry considerations played a large part in early structure analysis and x-ray studies were at first confined almost entirely to inorganic compounds, the crystals of which often possess high symmetry This work was of immense significance since it made possible the systematization of a vast part of inorganic chemistry, the molecules of organic chemistry, which generally possess little or no symmetry, remained for some time almost immune from attack

THEORETICAL BACKGROUND

The object of the x-ray analysis of a crystal is to determine, as accurately as possible, the positions of the atoms within the unit cell, that unit, which by translational repetition in three dimensions, builds up the crystal The observations which are available for this purpose consist of the directions and intensities of the set of diffracted beams produced when the crystal is exposed to x-rays For a given wavelength of x-rays, diffraction occurs in certain definite directions which depend only on the dimensions of the unit cell, the intensities depend, however, not only on the angle of scattering, but also on the nature and distribution of the scattering matter within the unit cell Just as each diffracted beam from a one dimensional grating may be designated by a single integer n, describing its order of diffraction, the diffracted beams from a three dimensional grating are designated by a number triple (hkl) Each diffracted hkl beam (or hkl reflection, since it can alternatively be regarded as being due to reflection of the x-rays from the crystal plane with Miller indices hkl) has associated with it a quantity $F(hkl)$ which describes both the amplitude and phase of the scattered wave This quantity is the resultant of the wavelets scattered by the individual atoms in the unit cell, combined vectorially, and it may be represented by the exponential function

$$F(hkl) = \sum_i f_i \exp 2\pi i(hx_i + ky_i + lz_i)$$

where f_i represents the scattering power of the ith atom and x_i, y_i, z_i are the coordinates of the ith atom expressed as fractions of the unit cell edges a, b, c and the summation is taken over all the atoms in the unit cell Now the observed amplitudes $|F(hkl)|$ can easily be obtained—they are proportional to the square roots of the intensities after appropriate corrections, and the amplitudes which would correspond to any given arrangement of atoms can be calculated The parameters x_i, y_i, z_i can be adjusted until the calculated values of $|F(hkl)|$ agree well with the observed values, and the best set of parameters obtained may be regarded as giving a fairly accurate description of the structure For inorganic structures where some, most, or sometimes all, of the atoms may be placed by symmetry, only a small number of parameters may be left to be determined in this way and the problem becomes feasible, but for the majority of organic crystals, so many parameters have to be adjusted simultaneously that the method becomes impracticable W H BRAGG, as early as 1915, suggested the use of Fourier series in crystal structure analysis and it is surprising that it was not until ten years later that the method was actually employed This method of analysis has proved to be the most fruitful but within the last few years other approaches to the problem have been made In 1941 E W HUGHES[1] adopted the procedure of regarding the quantity

$$\sum_{hkl} \omega \{ |F_{obsd}| - |F_{calc}| \}^2$$

as a function of the parameters and minimizing it by the method of least squares, and more recently A D BOOTH[2] has suggested the use of steepest descents for minimizing analogous quantities For these minimization methods to converge to the correct structure it is necessary to have, as a starting point, an approximately correct structure These techniques do not appear to have been employed widely, perhaps owing to the somewhat earlier development of the Fourier method of analysis

The electron density distribution throughout the crystal is a periodic function and it may be expressed as a triple Fourier series

$$\rho(xyz) = \frac{1}{V}\sum_h \sum_k \sum_l |F(hkl)| \cos[2\pi(hx+ky+lz) - \alpha(hkl)]$$

where V is the volume of the unit cell The quantities $|F(hkl)|$ and $\alpha(hkl)$ are, respectively, the amplitudes and phases of the diffracted beams The amplitudes can be obtained experimentally as has been mentioned above but, unfortunately, no experimental method is available for the determination of the phases The phases must be found by some indirect process, so that one cannot proceed in a straightforward manner from the observations directly to the conclusions The problem of determining the phases is, in fact, the crucial problem of x-ray structure analysis, and one which can only be solved relatively infrequently

If an approximate structure, giving reasonably good agreement between the observed and calculated values of $|F(hkl)|$, can be derived in some way or other, it is possible to refine this by the Fourier series method A series is summed, using the observed values of $|F(hkl)|$ and the calculated values of $\alpha(hkl)$ Since the calculated amplitudes are approximately correct it may be assumed that the calculated phases are not very far from the true values In the resultant electron density map, the centres of the peaks of electron density are associated with the positions of the atoms in the cell, and may be measured These new parameters can be regarded as more accurate than the original ones since they depend, to some extent, on the observational data, and the values of $|F(hkl)|$ calculated from these will agree more closely with the observed values If high accuracy is desired, the new structure can be regarded merely as a better approximation and the procedure outlined above can be repeated until the phases no longer change with each successive Fourier series It must be pointed out that the computation of even one three dimensional Fourier series, containing perhaps 1,000 terms, entails a prodigious amount of labour It has often been considered as more convenient to make use of two dimensional Fourier series which contain far fewer terms, and which give the electron density projected down a particular direction in the crystal One other simplification is of considerable importance, in general the phase to be associated with any reflection may have any value from 0° to 360°, but if a centre of symmetry is present in the crystal and is taken as the origin of coordinates, the phases are limited to the values 0° or 180°, so that our ignorance of the phase is replaced simply by our ignorance of the sign (+ or −) of the reflection

The problem of determining the phases can be solved, then, if some approximately correct structure is available, and we must now consider some methods of deriving such a structure It must be stressed that for the majority of crystals this cannot be done by present methods, there is no hard and fast procedure and every investigator in the field has his own method of attacking a crystal structure

TRIAL STRUCTURE

Trial and error methods of approaching the correct structure have been used to a considerable extent A molecular model is derived on the basis of chemical knowledge, past experience of similar structures, the optical and magnetic properties of the crystal *etc* Some position and orientation of such a molecule in the unit cell is assumed and the values of $F(hkl)$ corresponding to such a structure are calculated If the amplitudes are approximately the same as those observed, the structure may be regarded as roughly correct and a closer approximation to the correct structure may be achieved by carrying out Fourier syntheses, or by the minimization methods mentioned earlier

DIRECT METHODS

This method of trial and error is essentially intuitive in its approach to the structure and a more direct approach may be provided by the calculation of the Patterson function The Fourier series

$$P(uvw) = \sum_h \sum_k \sum_l |F(hkl)|^2 \cos 2\pi(hu + kv + lw)$$

into which the unknown phases do not enter, gives the electron density at $(x + u,\ y + v,\ z + w)$, averaged over all points (xyz) The function $P(uvw)$ can have a high value only if the electron density both at some point xyz and at $(x + u, y + v, z + w)$ is large The information provided is thus not about the distribution of the atoms themselves, but rather

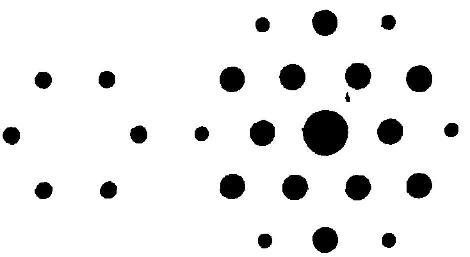


Figure 1 Corresponding to the hexagonal array of points shown on the left, the Patterson vector diagram is shown on the right. The large peak at the origin represents the fact that every atom is at zero distance from itself, the other peaks are drawn in two sizes, according as to whether one or two interatomic vectors terminate there

about the distribution of interatomic vectors (*Figure 1*). The Patterson function represents the maximum amount of information which can be obtained directly from the observations, but there is one serious drawback to its general utility. The function can be interpreted in terms of the interatomic vectors only if the peaks which correspond to these vectors are individually resolved. It is not necessary that all the peaks should be resolved but unless a considerable number can be identified the interpretation is impossible. But for *n* atoms in the unit cell there are $n(n - 1)$ interatomic vectors, the volume of the cell is approximately proportional to *n* so that as *n* increases the density of interatomic peaks increases proportionately and it becomes more and more difficult to resolve the individual peaks. Because of this it is not in general possible to interpret the Patterson function of a crystal which contains more than about 30 atoms in the unit cell. Modification functions to sharpen the Patterson peaks have been proposed and, with their use, it might be possible to double this number. The three dimensional Patterson function seems to have been calculated for only a very few crystals, and to have been successfully interpreted for only one[8], the aminoacid *l*-threonine $CH_3CH(OH)CH(NH_2)COOH$. This crystal contains four molecules in the unit cell, which thus contains 32 atoms (excluding hydrogen atoms which have only a very small effect on the x-ray scattering) and although a sharpened Patterson function was calculated the interpretation, although finally achieved, was found to be difficult owing to poor resolution of the peaks. Some protein molecules appear to display considerable internal order, and in these a large number of interatomic vectors may be almost identical. The peaks which appear in the Patterson function may be the resultant of several thousand closely similar interatomic vectors and although these vectors cannot be individually identified the broad features of the structure may be deduced. This has been done for haemoglobin, and the reader is referred to the detailed account in an earlier article in this journal[15]. Patterson functions projected down one of the crystal axes have been calculated for many crystals, but they are subject to even more severe limitations and can be considered as useful aids to the analysis only in very special circumstances.

The above discussion refers to a crystal in which all the atoms are of about the same scattering weight. If one or two atoms of outstandingly great atomic number are present the vectors between these stand out very clearly and the positions of such atoms can thus be fixed with great ease. This is of the utmost importance since, if the positions of the heavy atoms are known, the contributions of these atoms to the total scattering can be calculated. The scattering power of an atom is approximately proportional to its atomic number, and the scattering due to the heavy atom is in phase, while that due to the light atoms present is out of phase, so that the contribution of the heavy atom effectively determines the magnitude and phase of $F(hkl)$. A Fourier series in which the coefficients are the observed values of $|F(hkl)|$ and the phases are those given by the heavy atom alone can be calculated and the resultant electron density map will show not only the sharp peak corresponding to the heavy atom but also diffuse regions of positive electron density which may be associated with the remainder of the molecule. Approximate positions for the other atoms may be obtained and the structure refined as described previously. In this way it is possible to determine the structure of a molecule with a minimum of chemical assumptions.

Closely associated with the heavy atom method is the method of isomorphous replacement. If, in the molecule, one atom A can be removed or replaced by a second atom B, of different atomic number, without an appreciable change in the crystal structure, the differences in the intensities of the reflections are due entirely to the different contributions of A and B to the total scattering. If the position of the replaced atom can be found, the magnitude and phase of this difference can be calculated and may serve to fix the signs or limit the phases of the $F(hkl)$'s.

To complete this survey of the methods of x-ray structure analysis mention must be made of a recent attempt by D. HARKER and J. S. KASPER[4] to obtain the phases of the x-ray reflections directly from the observed data. It was shown that the application of certain inequality relationships to the formulae for calculating $F(hkl)$, leads to the establishment of inequalities between some of the $F(hkl)$'s. These are in the form of relationships between the magnitudes of some of the $F(hkl)$'s and the signs or phases of others, if the magnitudes are known, limitations may be imposed on the signs and phases. This method has already been applied to the determination of the structure of oxalic acid dihydrate directly from the observed data[5] but it has been shown by E. W. HUGHES[6] that the method becomes less and less powerful as the number of atoms in the cell increases, and that it will fail completely when applied to complex molecules.

EARLY STRUCTURE ANALYSES

The description of the structure of a molecule can be considered as falling into two parts: first, the description of the topological configuration and secondly, the description of the dimensions. For the most part, x-ray crystallographers have limited themselves to determining, as accurately as possible, the dimensions of fairly well known molecules, accepting as a starting point, and subsequently confirming in the course of the analysis, the configuration as determined by classical chemical methods. This limitation was imposed largely by the indirect nature of the methods at their disposal, trial and error followed by Fourier series refinement and the impossibility, generally, of a more direct analysis.

An enormous amount of information on interatomic distances and valency angles has been collected and, although the precision of these measurements has often been overestimated, most of it can be regarded as accurate to within a few hundredths of an Ångstrom unit and one or two degrees. Incidental to this, much of the detailed stereochemistry of molecular structures has been derived for the first time. The tetrahedral carbon atom, postulated by J. H. VAN'T HOFF and J. A. LE BEL to account for the observed facts of optical activity, had proved so successful that many chemists considered that the tetrahedral configuration was maintained in all organic compounds. In 1929, however, K. LONSDALE showed that the molecule of hexamethylbenzene was planar to within the limit of error of her experiments, and shortly afterwards J. M. ROBERTSON demonstrated the planarity of a whole series of aromatic hydrocarbons, naphthalene, anthracene, durene, benzoquinone and others. It was further shown that a system of two single bonds and a double bond about a carbon atom was planar, and that a single bond-triple bond system was collinear. This type of information, together with a knowledge of the interatomic distances involved, has been of great significance in the development of modern theories of the chemical bond[7].

With the more powerful methods of analysis available today, it is possible to determine the configuration of quite complex molecules. This was indeed possible to an even more limited extent in the earlier days of x-ray crystallography. For example, the configuration of hexamethylenetetramine was established by x-ray methods as early as 1923, but this was possible only because the crystals, as well as the molecules themselves, possess a high degree of symmetry. Again, information about the approximate shape and dimensions of molecules was sometimes deduced from incomplete x-ray analyses comprising the determination of the unit cell size and space group, together with the optical properties of the crystals. The then accepted structure for the sterol skeleton was found by J. D. BERNAL to be incompatible with such x-ray measurements and his investigations were of considerable value in arriving at the correct structure. E. G. COX contributed similarly to the determination of the structures of the sugars and was able to establish the structure of ascorbic acid (vitamin C) by x-ray analysis.

The most striking contributions of x-ray analysis to our knowledge of the configurations of complex molecules depend, however, on the development of the method of isomorphous replacement and of the heavy atom technique. The simultaneous investigation of phthalocyanine and of its nickel salt by J. M. ROBERTSON in 1936 led to the structure determination of this very complicated molecule by x-ray methods alone, without the necessity of making any previous chemical assumptions about its structure. This was soon followed by the analysis of platinum phthalocyanine where the heavy platinum atom, situated at a centre of symmetry in the crystal, completely determined the sign of every reflection. Since this work, the use of these methods has increased year by year and has already led to some significant increases in our knowledge of the detailed molecular structures of many types of molecules.

RECENT STRUCTURE DETERMINATIONS

Continuing the earlier work on sterols, C. H. CARLISLE and D. CROWFOOT succeeded in determining the structure of cholesteryl iodide[8], their results in the main confirmed the previous views concerning its structure, but they were able to provide definite evidence on some doubtful stereochemical points. The analysis of a calciferol derivative, the 4-iodo-5-nitrobenzoate by D. CROWFOOT and J. D. DUNITZ[9] has cleared up one major point of difference between the previous chemical and crystallographical evidence on the structure of this compound. In the usually accepted chemical structure for calciferol (vitamin D) ring *A* is joined by a short chain to ring *C*. While the formula is usually written in the manner shown in *I* to show its similarity to the other sterols, it

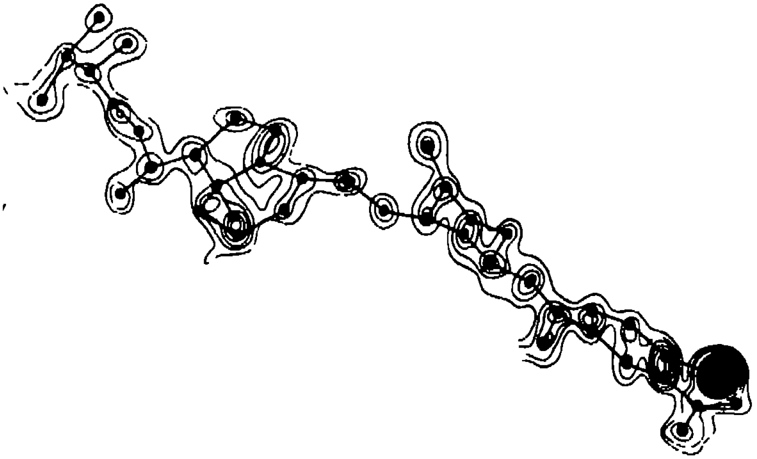
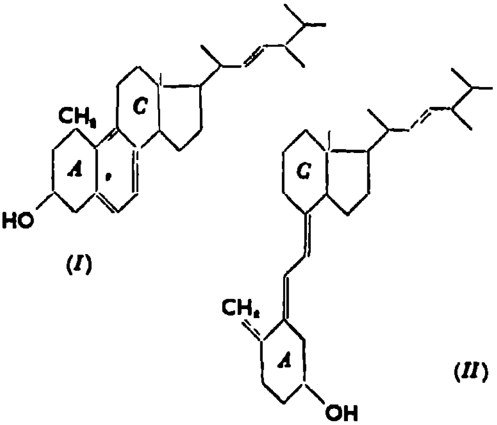


Figure 2 Fourier projection of iodonitrobenzoate derivative of calciferol

seemed highly probable that such a molecule would adopt the configuration shown in *II* The shape of this molecule would therefore be expected to differ considerably from that of the normal sterols, but the previous crystallographic evidence showed that the unit cells of calciferol and its derivatives did not differ radically from those of other sterols This was interpreted as evidence that calciferol could not have the extended structure shown in *II* Moreover, the fact that calciferol could be obtained so easily from ergosterol and could be converted so easily into pyrocalciferol, both normal sterols, suggested that calciferol itself could not differ greatly from these molecules The crystal structure analysis of the iodonitrobenzoate derivative demonstrates conclusively that the molecule does indeed have the extended configuration, at least in this compound, as shown in the projection (*Figure 2*) The relationship of the molecules to the crystal axes is, however, very complicated and shows that it may be dangerous to draw conclusions concerning shapes and dimensions of molecules from the unit cell dimensions alone



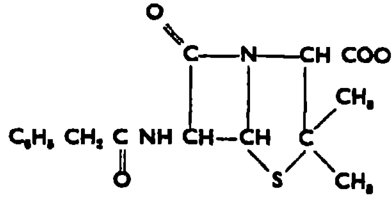
(*I*)

(*II*)

The early work on the structures of sugars has culminated in the complete structure analysis of the sucrose molecule[10] The attempt to analyse sucrose itself by the Patterson method proved to be unsuccessful, but C A Beevers and W Cochrane were able to apply the isomorphous replacement method to the molecular compounds which sucrose forms with sodium chloride and bromide ($C_{12}H_{22}O_{11}$ NaBr $2H_2O$) to show that sucrose was *d*-glucopyranosido *d*-fructofuranoside, confirming the chemical evidence The pyranose ring is of the expected Sachse *trans* form and the furanose ring was shown to be non-planar, one atom being out of the plane of the other four

PENICILLIN

The successful analysis of the structure of penicillin is perhaps the outstanding accomplishment of the method of x-ray crystallography up to date This work has already been reviewed in this journal[11], and it will only be mentioned here that the final results for sodium and potassium benzylpenicillin show conclusively that the molecule is one of the stereochemical forms of the *β*-lactam structure



(*III*)

MOLECULAR COMPOUNDS

Molecular compounds constitute a field where the characteristic methods of classical chemistry are largely inoperative owing to the fact that most of these compounds exist only in the solid state Both H M Powell and D H Saunder[12] and their collaborators have studied the complexes between poly-nitro compounds and other aromatic hydrocarbons and have shown that no chemical binding, in the usual sense, exists between the components In the complex trinitrobenzene-*p*-iodoaniline, each type of molecule occupies a separate layer in the crystal, the distance between the layers corresponding not to chemical bonds but merely to van der Waals interactions An interesting new aspect of molecular compound formation has been discovered recently by H M POWELL and D E PALIN in what are called clathrate compounds They have shown that in certain complexes formed by quinol with other molecules, the quinol molecules are linked by hydrogen bridges to form two interpenetrating three dimensional cage structures extending throughout the crystal Two giant molecules are thus formed These are not directly linked with each other, but nevertheless they cannot be separated without the severance of their own structure The framework formed is fairly open in character and it contains comparatively large cavities, which may be occupied by the second component of the molecular compound which is thus not chemically bound to the quinol molecules but is merely trapped in the cages formed by them The second component must therefore be small enough to fit into the cages and the complexes have been obtained only with small molecules, such as sulphur dioxide, carbon dioxide, and methyl cyanide A crystalline modification of quinol itself containing empty cages has also been isolated For further details of these fascinating complexes, the reader should consult H M POWELL's own review[13]

PROTEINS

The present x-ray studies on the macromolecules, such as the proteins which play so large a part in the organization of living matter, are, as yet, only at an embryonic stage Interesting speculations have been made by W T ASTBURY, based on the limited data available from protein fibres, but these structures are so complex, and the data available so scanty, that we are far from an understanding of their nature At the other end of the scale, the molecular structure group of the California Institute of Technology have made intensive studies of the units of which proteins are formed, the aminoacids and peptides[14], with a view to obtaining some knowledge of the principles which govern the building up of these units to form macromolecules At an intermediate stage, some x-ray studies have been carried out on certain crystalline proteins Perhaps the most interesting of these is the work of M F PERUTZ[15] and his co-workers on haemoglobin This protein has a molecular weight of about 70,000 and contains therefore about 5,000 atoms (excluding hydrogen) The molecule possesses, however, a twofold axis of symmetry, so that the placing of 2,500 atoms would, in fact, define the structure The intensities of about 7,000 reflections have been recorded in the course of the analysis but these, even if their phases could be determined, do not constitute sufficient information to give a complete solution of the problem, in the sense of resolving the individual atoms in a three dimensional Fourier synthesis For atoms to be resolved thus, the spacing limit of the recorded reflections must be about 1 2 Å, while in haemoglobin the limit is about 2 5 Å This difficulty is important when dealing with such complex structures and makes an accurate structure determination, such as can be obtained for simpler compounds, impossible The position of the molecule as a whole may vary considerably within the unit cell and the disorder introduced causes the reflections to fade out completely at a certain spacing limit M F Perutz has been able to deduce that the haemoglobin molecule has the approximate shape of a cylinder, of radius 28 5 Å and of height 36 Å, that the polypeptide chains appear to be arranged in 4 layers and to be parallel to one another, except where they bend back on themselves, he has also been able to draw interesting conclusions concerning the distribution of liquid of crystallization (which seems necessary for the specific orientation of macromolecules) in the crystals, and the orientation of the haem groups The complete structure analysis of a molecule as large as haemoglobin seems, however, only a remote possibility at the present stage

SUMMARY

The methods which are at present available to the x-ray structure analyst are quite adequate to solve, or at least to aid in the solution of, many of the problems of organic chemistry Much of the present day theoretical chemistry rests on the results of x-ray analysis, and valuable contributions have been made by the method to structural organic chemistry, particularly in the sugar and sterol fields, the present structure for penicillin is due mainly to the x-ray evidence Application of the method to other structural organic problems, such as the alkaloids, strychnine and colchicine particularly should produce important results The heavy atom method has proved to be the most powerful tool in solving complex problems of this type and so far it has never been pushed to its limit If suitable crystals can be prepared it seems quite within the bounds of probability that careful comprehensive studies on heavy-atom derivatives of at least the smaller proteins, such as the protamines, should lead to direct and fairly complete determinations of their structures, although the scale of such a problem would be of a vastly different order of magnitude to those structures which have been solved up till now

This paper constitutes Contribution No 1286 from the Gates and Crellin Laboratories of Chemistry

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Research and Cocoa Production

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COCOA, which is mainly consumed in the form of chocolate, may not rank as one of the world's major foodstuffs, but it is an important commodity and could be more so As a popular flavouring and sweetmeat it makes a useful contribution to diet by increasing the palatability of other foods, and unlike most substances used primarily for flavouring it is also of high nutrient value, the dried cocoa 'bean' containing about 50 per cent of fat as well as considerable quantities of carbohydrates and proteins

There is no doubt that if cocoa were plentiful much more of it could be used As it is, consumption is nearly 700,000 tons (tonnes) a year and the immediate problem is to maintain supplies at that level They are, on the most optimistic view, only precariously in balance with demand, and acute shortage might easily develop Analysis of the reasons may serve to show how research can help to realize the wider potentialities of the crop

REASONS FOR PRESENT POSITION

The most obvious cause of shortage is the spread of plant diseases Particular attention has been drawn recently to the ravages of swollen shoot on the Gold Coast, and this is the most serious menace because West Africa is the biggest producing region Though less alarm was created outside the countries affected, the appearance of witches' broom in the American tropics some 30 years ago was quickly followed by a decline in production, first in Ecuador and later in Trinidad, to a quarter of what it had been previously The effect has been not only to reduce yields but also to discourage increase in the acreage under cocoa There is thus good reason to put diseases high on the list of causes of scarcity

Diseases, however, often take the whole blame for disasters in which they are not the only agents, though they may be the most spectacular Most of them can be controlled—at a cost and there are in the tropics research services able to diagnose causes and suggest remedies—though not necessarily easy ones The spread of witches' broom in tropical America led to spectacular disaster chiefly because most of the growers had neither the heart nor the resources to apply the control measures recommended at an early stage Cocoa fetched heartbreaking prices in the middle years between the wars, and the West Indian grower lost faith in the future of the crop

In the present campaign against swollen shoot the question of financial resources is much less prominent and there are totally different reasons for lack of wholehearted cooperation by the growers Yet many of the difficulties in effecting control of the newer disease are similar to those encountered earlier in attempts to check the spread of witches' broom They are difficulties inherent in the conditions under which cocoa is grown , and those conditions, created partly by economic causes and partly by lack of scientific knowledge, are the less obvious but fundamental reasons for the state of the industry

Economic circumstances have favoured extensive planting of cocoa as a single crop rather than intensive culture within balanced systems of agriculture Available labour can usually give little attention to the trees beyond harvesting, and though this system keeps costs low in the absence of disease, it renders most of the recognized methods of control almost impossible

Lack of scientific knowledge tends to be obscured by the gap between available information and average practice, but it is an important factor in the situation In the first place, the cocoa tree as generally grown is a relatively inefficient producer for want of scientific breeding and consequently incapable of responding profitably to really intensive cultivation This fact is as fundamental as any, and genetical studies leading to improved planting material are the necessary foundation of increased production Beyond that, even the mediocre possible performance of available material is reduced by ignorance of its physiology and of the measures necessary to maintain soil fertility under the conditions imposed by plantation agriculture It is significant that in all the older cocoa growing countries, including those with the highest standards of management, declining yields were noticed before the advent of major diseases

CONDITIONS OF CULTIVATION

Cocoa in its natural habitat is a small tree in one of the lower tiers of vegetation in tropical rain forest, where it grows in shade and high humidity with complete protection from wind and indeed from all air movement but the gentlest These are not necessarily ideal conditions for a commercial plantation, but they provide some guide to the requirements of the species, and it has always been the general aim of planters to re-create an environment resembling the forest to some extent

The most important characteristic of forest conditions would appear to be their relative equability, particularly in water relations Cocoa trees will survive a moderately severe dry season if suitably protected so that their loss of water by transpiration is held fairly steady but they are highly intolerant of violent fluctuations in water balance, such as occur on exposed sites where sun and wind may cause excessive transpiration even when the soil is moist Both shade and lateral protection help to damp out fluctuations, and of the two the lateral protection is perhaps the more important

Experience in cultivation has shown that shade is not essential for bearing cocoa trees, but in most climates it is beneficial and is commonly provided either by the planting of special shade trees or by leaving suitable wild trees standing when forest is cleared for planting Experience has also shown, however, that too dense a shade will reduce cropping

Protection from wind is achieved partly by selection of site but much more often by massing the trees Distance of planting varies in different countries from 4 ft up to 20 ft (1 2–6 1 m) apart and even at the widest spacings the fully grown trees interlace to form a continuous canopy of foliage Where wide distances are adopted shade trees are always planted, and, conversely, where no shade is provided a close spacing is always used and the canopy closes in more quickly Gaps in the canopy, however caused, usually lead to trouble, and the isolated unshaded tree will flourish only under special conditions of lateral protection

Though able to withstand several weeks of dry weather at a time, cocoa trees need a good supply of water to the roots for the greater part of the year, and are therefore grown on rainfalls rarely lower than 50 in, often between 60 and 80 in, and sometimes well over 100 in a year (respectively, 1,270, 1,524, 2,032 and 2,540 mm) At all these levels, and especially at the higher rainfalls, there is inevitably excessive moisture at some seasons

Hence, one of the basic problems of cocoa growing is to strike a balance between too dense a canopy, encouraging fungal diseases in the wet season and reducing yield by excessive shade, and too much exposure, leading often to insect attack and always to die-back and general debility in dry weather To achieve the best results drainage, windbreaks, planting distance and the provision or non-provision of shade have all to be integrated, and continual adjustments by pruning, thinning or supplying gaps are necessary

It must be added that cocoa is one of the more exacting species in its demands on the soil, and though plantings on inferior soils may often show promise in the early years, yields are only maintained on good soils properly treated As the crop is commonly grown without any manuring at all, it is scarcely surprising that all but the best soils show declining yields after a time

For all these reasons cocoa is by no means an easy crop to grow, even in the absence of major diseases The huge production built up in West Africa by native farmers with no previous knowlege of the tree was due to many factors favourable to the rapid expansion of the industry in the early years of this century difficulties began to appear before production reached its peak and disease has accentuated them, but did not create them

POSSIBILITIES OF INCREASING PRODUCTION

It is clear that no increased production is to be expected from existing cocoa areas without control of the major diseases, for in districts where either swollen shoot or witches' broom is rampant additional planting without prior control would be futile

As a measure of insurance for the near future, new planting is being encouraged in countries where the major diseases do not occur, with precautions against their introduction The new areas will in any event be useful, but on account of the special requirements of the tree it is doubtful whether enough of them could ever be found to meet world requirements if the diseased areas of West Africa and and tropical America went entirely out of production Unflagging efforts to control disease in the older areas therefore remain essential

Once control is achieved, emphasis will shift to other aspects of productivity The average crop over the whole of the producing areas at present is probably less than 500 lb per acre (560 kg/hectare) per annum, a level at which cocoa must be a semi-luxury product Full application of past research could double the average yield a reasonable aim for further research would be to quadruple it

There is no essential difference in aim between investigations connected with immediate disease control and the more fundamental work needed to put cocoa production on a better foundation The ultimate answer to pathological problems will not lie entirely in palliative measures against fungal parasites and insect pests It will be found partly in new strains of cocoa with more inherent resistance to attack and sufficiently productive to respond to intensive culture, and partly in new cultural methods based on physiological knowledge

CONTROL OF DISEASES

The major diseases have received much study already, and enough is known about them to indicate the most promising methods of control, so that present research is concerned largely with overcoming technical difficulties in application

Swollen shoot is a virus disease, about which a highly creditable amount of information has been collected by the workers at the West African Cocoa Research Institute They have found that at least a dozen viruses are involved, some perhaps only strains but others distinct and unrelated Indigenous West African species of the families Bombacaceae and Sterculiaceae carry them and are presumably the source from which the cocoa was originally infected[1] The different viruses produce different symptoms on cocoa, and some are much more virulent than others They are carried from cocoa to cocoa, and from wild trees to cocoa, by various species of mealybugs, which feed on a wide range of plant species

Cure of infected individual trees is not reckoned among immediate possibilities The disease must be fought by checking spread of infection, and as the vectors are difficult to attack, practical control aims at reducing the centres of infection This means cutting out all diseased trees, both cocoa and forest species, in the neighbourhood of cocoa

One essential for control is early recognition of the disease, and the earliest symptoms are only inconspicuous markings on young leaves at a certain stage of development They have been studied and described on cocoa by grafting diseased buds into healthy seedlings and so infecting them The symptoms on wild species are still more obscure, and the presence of virus can often be detected only by transferring it to cocoa through infected mealybugs The identification of indigenous carriers of virus is still a matter for continuing research

As some of the wild hosts are huge trees, very difficult to destroy economically, research includes trials of chemical methods of arboricide It also includes investigations of the recently introduced systemic insecticides, which may help to give a partial control of the vectors

Witches' broom has been studied at the Imperial College of Tropical Agriculture and by the Department of Agriculture of Trinidad and Tobago It is caused by a fungus, *Marasmius perniciosus* Stahel, and is named from the hypertrophied growths produced when the spores of the fungus infect developing shoot-buds , but its most damaging feature is a pod rot caused by infection of growing fruits Control again depends on reduction of centres of infection, but with a difference It is not, in theory at least, necessary to cut out infected trees, but only to remove from them all infected shoots and fruits in order to prevent fructification of the fungus In practice, where old trees are severely infected, the complete excision of infected tissues is so expensive that felling and replanting may be more economical

Excision is the only method of control yet established Spraying, unless new methods can be found, is impracticable Good hopes, however, appear to lie in the use of some highly resistant strains of cocoa discovered by the late F J POUND[2] in the Upper Amazon basin

Before either of the two major diseases became prominent heavy losses were incurred from black pod, another fungal disease characterized by rotting of fruits and cankering of branches, caused by *Phytophthora palmivora* Butler This disease is universal and has never been brought well under control where climatic conditions favour it There are several other pod rots and various root diseases of more local significance in different countries

There are also several insect pests of major importance that have received some study but require more, notably capsid bugs in West Africa and thrips in Trinidad The total annual loss of cocoa from diseases and pests is not known, but it is probably an amount which, if saved, would remove all immediate danger of scarcity.

IMPROVEMENT OF PLANTING MATERIAL

The possibilities of increasing the productivity of cocoa plantations by scientific plant breeding are very great indeed. The species is indigenous or of ancient introduction over a wide area from Mexico to Peru and highly variable over its range[3]. The Trinitario cocoas of Trinidad, Venezuela and the Caribbean region generally are particularly diverse, and even in a single field types can be found as different from each other as are (to take a familiar species for comparison) the apple varieties of Europe.

Plant breeding and genetical observations have not yet gone far beyond simple selection in the heterogeneous Trinitario population, but even simple selection, coupled with vegetative propagation, has isolated clones yielding at least two or three times as much cocoa per acre as the unselected population. The clones also demonstrate striking differences in habit, degree of resistance to diseases and pests, and quality of product, that can be turned to good account. The combination of desirable characters by crossing and re-selection is now under way, and should result in cocoa varieties far more efficient as crop plants than any available previously.

This is only the beginning. The variation among Trinitario cocoas is only a fraction of that immediately or potentially available to the breeder. The botanical study of cocoa started late, and representative collections of breeding material have not long been available, but the lack is fast being remedied. Mention has been made of the discovery by Pound of a high degree of resistance to witches' broom among Upper Amazon cocoas never before in cultivation. A reservoir of Upper Amazon material has still to be examined for other useful genes, and there are large areas (notably the Orinoco basin) from which the native cocoas have not yet been collected for study. Beyond that again are possibilities of using other species of *Theobroma* in interspecific crosses.

The potentialities, in cocoa, of breeding for increased yielding power are important because they vitally affect the future of cocoa growing. More intensive cultivation has been rendered inevitable by the major diseases, which can only be controlled by processes demanding continuous application and a higher standard of skill in the grower. Genotypes are required capable of profitable response to intensive treatment, suited to the new ecological conditions created by new systems of culture, and acceptable in the quality of their product. The evidence indicates that they can be bred.

IMPROVEMENT OF PLANTING METHODS

Improving planting methods calls for researches embracing physiological investigations including nutritional needs, soil studies, and agronomical experimentation. It is essential for the rationalization of planting systems that more should be known about the functions of shade. Shade undoubtedly affects transpiration and hence the whole water balance of the tree; it also affects photosynthesis thus bearing on nutrition. The complex interactions of shade, protection, nutrition and water supply will take a lot of working out, and fundamental knowledge must be gained from study of the physiology of the leaf before optimum conditions can be arranged in the plantation. There is scope for fruitful collaboration between physiologist and geneticist in studying the reaction of various genotypes to different degrees of insolation with a view to effecting the best adjustment between type and environment.

Study of cocoa soils is a special aspect of nutrition requiring its own team of workers in collaboration with the physiologists. Here again good foundations have been laid[4] but much remains to be done and the great need is for more manpower to intensify research.

The cocoa agronomist has perhaps the most complicated role in the research team, as it is his business to find the most economical applications in the field of the findings of the laboratory. In established plantations his scope is necessarily limited, and there can be no sudden revolution in plantation methods, since all the circumstances of the industry are against it. We are concerned, however, with the long view. The planting of new areas and replanting of diseased areas will open up big opportunities if answers can be found to a number of questions, of which only a few can be mentioned.

How far can necessary protection from excessive air movement be obtained with tree arrangements permitting the use of mechanized equipment for disease control? What is the possible place of cocoa on mixed farms where livestock provide organic manure for the trees? Can this tree crop, by the use of material selected for early bearing, be fitted into a long term (say 25 year) rotation of crops with advantage to the soil? What are the possibilities of interplanting cocoa with other tree crops to eliminate the unproductive shade tree? These are all questions of applied ecology, and though they may be answered by empirical trials they are intimately connected with the basic inquiries into genetics and physiology.

IMPROVEMENT OF PREPARATION

The 'wet' cocoa harvested from the tree is fermented and dried on the plantation to make the marketable product, and this preparation affects both cost and quality. It constitutes another fruitful field of research in which microbiology and biochemistry are the basic sciences involved. The Colonial Microbiological

Research Institute in Trinidad is working in this field with the Imperial College of Tropical Agriculture interested in some aspects of it, and both institutions keep close contact with research organizations of the chocolate manufacturing industry which are naturally very much concerned with the question of quality, as they are indeed with all aspects of cocoa production

SUMMARY

Present world supplies of cocoa are barely enough to meet an immediate demand which is itself much lower than potential demand Examination of the conditions under which cocoa is grown shows that, although the obvious threat to supplies comes from plant diseases, there are deeper underlying reasons for the precarious state of the industry Improved supplies and a stable future for the grower depend on more efficient production, towards which research must contribute by both *ad hoc* and more fundamental investigations

In the sphere of plant pathology research is most urgently necessary for overcoming technical difficulties in the application of control measures, though there is also need for much more information on diseases and pests For improvement over a longer term we have to look to genetics and plant breeding for more efficient planting material, responsive to intensive culture, to plant physiology and soil science for elucidation of the principles underlying planting methods, and to agronomy for the economical application of those principles in the field Microbiology and biochemistry are involved in parallel researches on the preparation of cocoa beans on the plantation, affecting their cost and quality

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Mercury in Chemical Metallurgy

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IN the technology of metal extraction the expression 'amalgam metallurgy' is new It was chosen[1] to describe comprehensively certain new processes developed at the Duisburg Copper Works[2] and extended with the aid of the I G Farbenindustrie A G during recent years Apart from a series of patents[3] of little significance and occasional comments in the literature[4] this work is hardly known Nevertheless, several pilot plants have been in operation, partially for some years, a full scale plant for the production of pure zinc from roasted pyrites by amalgam metallurgy was being built but was not completed before 1939

The way for amalgam metallurgy has been prepared by two predecessors the Castner-Kellner process for electrolysis of alkali chlorides using mercury cathodes[5] to which is due the large scale development of the use of costly and poisonous mercury as an intermediate in heavy chemical industry, and polarography[6], the method of analysis by the dropping mercury electrode from which current/voltage curves yielded important information on the behaviour of amalgams and the reactions occurring at the phase boundaries of amalgams in aqueous solution There are of course occasional references in earlier patent literature relating to heavy metal amalgams which may be considered as historical forerunners of amalgam metallurgy, but they are impractical and comparatively useless[7]

As with wet extraction, amalgam metallurgy constitutes a further invasion of metallurgical processes by chemical technology, whereby coarse high temperature reactions are replaced by exactly controllable reactions in the cold, for mercury introduces the possibility of obtaining different metals in the form of very dilute amalgams, reactive and liquid in the cold Amalgam metallurgy enables low grade complex ores and even inferior raw materials to be used, since the cheapest form of decomposition gives a direct yield of valuable metallic end-product, such as the purest form of metal or alloy powder used in metal ceramics

Low grade ores[8] are unsuitable for normal metallurgical processes since the predominating content of gangue requires too much fuel for extraction procedure and leads to considerable loss of metal in the slag Even flotation, specially suitable for working poor ores, is often uneconomic *It* is characteristic of amalgam processes that the achievement of high purity is particularly easy and cheap, a particular type of this new wet metallurgical technique, the so-called barrier electrolysis, yields highest purity metal from grossly impure metallic salt solution in one stage, without additional processes or purification *i e* without extra cost by this process it is impossible to produce anything but the highest quality metal

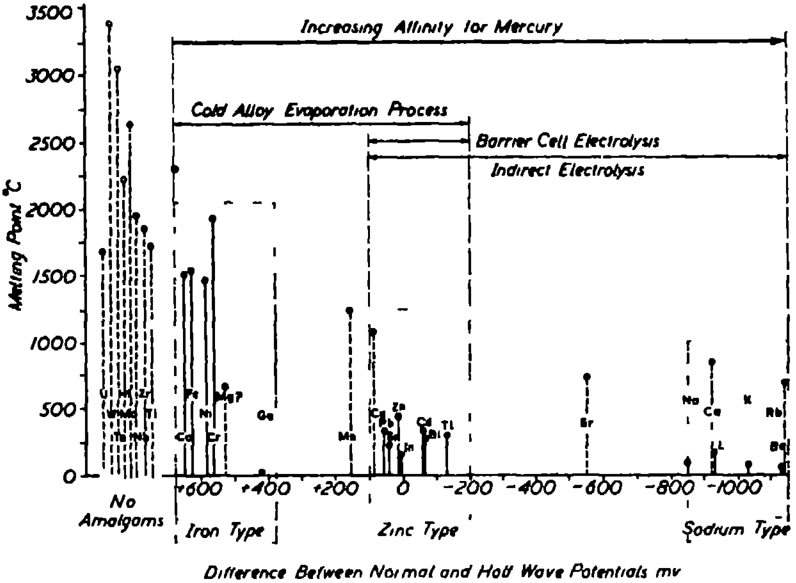

Figure 1 *Types of amalgams*

The greater applicability of alloys compared with individual metals justifies relatively costly production processes for example with the aid of expensive high frequency vacuum furnaces, and with high wear and tear on melting pots Thus the market value of alloys is always higher than that of unalloyed metals Since the amalgam technique enables alloys to be prepared with the same expenditure of work as for pure metals, direct from the ore without preparing the individual metals

The difference between the market value of semi-finished products and of the metal itself is considerable for all metals and depends on the manner of working, such as thickness of sheet, diameter of wire *etc* The starting material for metal ceramics, powdered metal which is usually prepared by sputtering the molten metal in air or water, by stamping and milling, by electrolysis or some other method[10], commands a much higher price as prefabricated metallic semi-finished product than as the solid metal, and may be obtained by a process well known in amalgam metallurgy, the dry mercury evaporation *i e* so-called *Schwelung* process Thus amalgam metallurgy can use low grade ores as starting material, particularly as the prices of high grade ores (*Table I*) often form the largest part of purification costs which are less for chlorinating decomposition processes

Table I *Pre-war Average Prices for Ores and Metals in Austria* (*Official Export Trade Statistics*)

Material	*Price Austrian schilling per ton*	*Metal*	*Price Austrian schilling per ton*	*Geochemical frequency per cent*
Iron ore	22 –	*Crude iron*	150 —	5 00
Zinc ore	60 –	*Crude zinc*	500 —	0 004
Rich manganese ore	120 —	*Ferromanganese*	450 —	0 1
Lead ore	220 —	*Soft refined lead*	490 —	0 0016
Antimony ore	400 —			0 0001
Calcined pyrites	20 —	*Crude copper*	1,200 —	0 01
Bauxite	45 —	*Crude aluminium*	2 500 —	8 15
Other ores	390 —	*Nickel*	5,500 —	0 01
		Tin	5,500 —	0 004
		Silver	108,000 —	0 00001
		Gold	6,200,000 —	0 0000005

TECHNICALLY IMPORTANT PROPERTIES OF AMALGAMS

Affinity of metals for mercury— It is useful to divide amalgams into three groups according to their technical applicability which can be designated by naming for every group one characteristic metal as the iron, zinc and sodium types (*Figure 1*) The amalgams of the iron type tend to be particularly useful for production of alloy powders, those of the zinc type for the preparation of pure metals and those of the sodium type as aids in working up solutions difficult to electrolyse

This division corresponds to three different degrees of affinity with mercury The greatest affinity is found in metals of the sodium type which unite with mercury with considerable evolution of energy, often explosively, to form stoichiometric intermetallic compounds Zinc type metals have a medium affinity, good miscibility with mercury without excessive heat production, and form mixed crystals Metals of the iron group are not mutually miscible with mercury, yet a certain affinity remains since these metals in the nascent state are attacked by mercury so that at least surface amalgamation occurs Certain other metals can never be combined with mercury

As will be shown, there are accurate electric potential values which serve to characterize quantitatively the mercury affinity of metals but thermal data cannot be used directly The solution enthalpies of molten metals in mercury, which are strongly affected by concentration unlike the solution enthalpies of salts in water but similar to the enthalpies of mixing organic liquids, have opposite signs for solution enthalpy and dilution enthalpy, at infinite dilution mercury solutions have zero solution enthalpy

Table II Saturated Mercury-metal Solutions, in per cent by Weight

Metal	*Type of Amalgam*	25 C *metal*	70 C *metal*
Tl	*Zinc type*	43	52
Cd	" "	6	20
Cs	*Sodium type*	3 5	4
Zn	*Zinc type*	2	6
Bi	" "	1 4	11
Pb	"	1 3	7
Rb	*Sodium type*	1 2	3
Sr	" "	1	1 8
Sn	*Zinc type*	0 6	4
Na	*Sodium type*	0 6	1
K	" "	0 4	1 8
Ba	" "	0 5	0 8
Ca	" "	0 3	0 7
Mg	*Mixed type*	0 3	0 7

It should not be overlooked that the melting points of metals also play a part, though with frequent exceptions, in division into amalgam types Metals of the sodium type have on the average the lowest melting points, zinc type metals come next while iron type metals have high melting points and those which do not form amalgams have very high melting points Gallium is an outstanding exception, although melting in the heat of the hand and, with its silvery white colour so similar to mercury, it is completely immiscible with it

SOLUBILITY OF METALS IN MERCURY

True solution and metallic suspension— It should be noted at once that the amalgam technique in metallurgy is concerned almost entirely with easily flowing amalgams, either true solutions of metals in mercury or very dilute amalgam sludges which in outward appearance and flow properties are scarcely distinguishable from pure mercury the metals are handled in the flowing state in the cold

Surprising confusion prevails in the literature on the solubility of many metals in mercury Since mercury is opaque and metallic suspensions in mercury are often extraordinarily fine grained, and even colloidal, it is clearly not always easy to recognize the heterogeneous nature of a free flowing dilute amalgam suspension Thus iron and other metals of the iron type are undoubtedly completely insoluble in mercury, though the data in the literature[11] vary between 0 1 and 10^{-18} per cent The fineness of a metallic suspension in mercury depends on the suspended metal, as for example with copper which is much coarser than nickel, and also on the mode of preparation Thus heterogeneous amalgams prepared electrolytically when the mercury is stirred during electrolysis, particularly by ultrasonics, will remain mobile, being fluid even at quite high metal contents

On the average the highest solubilities in mercury are shown by metals of the zinc amalgam type, of which thallium has the highest value over 40 per cent at room temperature Metals of the sodium type have slightly lower solubilities It must be remembered that as a result of the high specific gravity of mercury, the volume content of mercury-metal solutions is much higher than would appear from the usual percentage figures for metallic systems, *Table II* A solubility of 1 per cent corresponds to 135 gm/l and the mol ratio of solvent to solute of a 2 per cent zinc amalgam corresponds to a half-saturated solution of sodium chloride. It is striking that the metals having good solubility in mercury occupy places next to mercury in the periodic table, both horizontally and vertically, this indicates a correlation between miscibility and the structure of the outer electron shells

The solubility of a metal in mercury always increases with rising temperature For the easily soluble metals of the zinc type it increases rapidly for even a small rise in temperature Thus a rise from room temperature to 70°C increases the solubility of bismuth eightfold, tin sixfold, lead fivefold and cadmium and zinc threefold It is understandable that the solubility of a given metal in mercury is generally greater the nearer the melting point of the metal is approached Thus the solubility of aluminium is very low at room temperature whereas at 550°C *i e* about 100C° below the melting point, it amounts to 10 per cent On the other hand iron and silicon, which at this temperature are still nearly 1,000C° below their melting point, still show a solubility about as low as at room temperature The example of gallium, quoted earlier, shows clearly that the nearness of the melting point to the solution temperature does not always lead to high solubility Just as in aqueous systems, the soluble and insoluble components can be separated from mercurial solution by filtration and sedimentation The precipitate does not sink the heavier mercury stays at the bottom while the precipitate floats on the surface like cream on milk Filtration is a means of separating the different groups of metals filtered amalgams are always free from metals of the iron type

There is another similarity between aqueous and mercurial systems, in that metals dissolved in mercury, especially by exchange between mercury and an aqueous phase, are readily and rapidly reactive, whereas metals not easily soluble are not easy reagents, insoluble, and cannot be exchanged Exchange between the mercury and aqueous phase plays an important part in amalgam metallurgy operations in preparing metals in purest form, insoluble metals of the iron amalgam type therefore cannot be prepared directly in pure form

Cold alloying—This inability to react does not govern all kinds of amalgam reactions, particularly not those for combination of components of the mercury phase between themselves Metallic suspensions in mercury are very often able to combine with soluble components in the amalgam, even at room temperature, thus precipitating them These precipitation reactions can be called 'cold alloying' The rate of reaction varies according to the nature of the insoluble component, being faster in nickel than in iron amalgam, often occurring with a notable evolution of heat in the reaction mixture, as in the combination of nickel and zinc Up to the present no example of cold alloying is known in which, at least, not one insoluble amalgam component takes part in the reaction Easily soluble metals coming together in mercury solution usually mutually raise their solubility Cold alloying, however, does not always occur when soluble and insoluble components are mixed in mercury Thus lead dissolved in mercury does not react with a suspension of cobalt amalgam though it does with copper amalgam, while cobalt amalgam will react at once with a mercury solution of cadmium

If metal suspensions in mercury, particularly those formed by electrolytic precipitation of iron or manganese at a mercury cathode, are filtered and the cake pressed, usually at high pressure and completely drained from mercury, great quantities up to 90 per cent or more of mercury are still retained On the other hand in multi-metal amalgams such as those prepared by cold alloying, the mercury content falls sharply In such alloy amalgams insoluble in mercury, the original amount of alloy component soluble in mercury can be precipitated by a fractional amount of the insoluble component *e g* one part of nickel will precipitate five parts of zinc

ELECTRIC POTENTIAL PROPERTIES OF AMALGAMS

Normal and half wave potentials—For all reactions of amalgams with aqueous solutions the potential difference at the mercury/water interface is decisive For a dilute amalgam the solution pressure of the metal dissolved in the mercury is proportional to its concentration, and the amalgam potential is

$$E = E_0 - \frac{RT}{nF}\ln\frac{C_{H_2O}}{C_{Hg}}$$

$$= K - \frac{0.058}{n}\left(\log C_{H_2O} - \log C_{Hg}\right) \qquad (1)$$

Where this formula shows that an amalgam potential does not alter if the mercury and water concentrations C_{Hg} and C_{H_2O} are changed in the same direction and in the same proportion, it is not necessary, in defining a characteristic normal amalgam potential, to let C_{H_2O} and $C_{Hg} = 1$ It is sufficient over quite a wide range if these two quantities are equal to one another As J HEYROVSKY and his co-workers have shown in their work[11] on the dropping mercury cathode, this occurs when a polarographic wave has reached its half amplitude These polarographic half wave potentials, which are independent of concentration, are an exact measure of the extent to which an amalgam of a given metal is electropositive or electronegative with respect to that of another metal, and by comparison of the normal and half wave potentials the concept of mercury affinity of the different metals can be defined exactly

The half wave potential can be extrapolated to the normal electrode potential, by letting $C_{H_2O} = 1$ and accordingly giving the highest possible value to the concentration in the metal phase, using

$$\varepsilon = -\frac{0.058}{n}\log\left(\frac{1000\varrho}{M} - 1\right) \qquad (2)$$

where n is the valency, M the molecular weight and

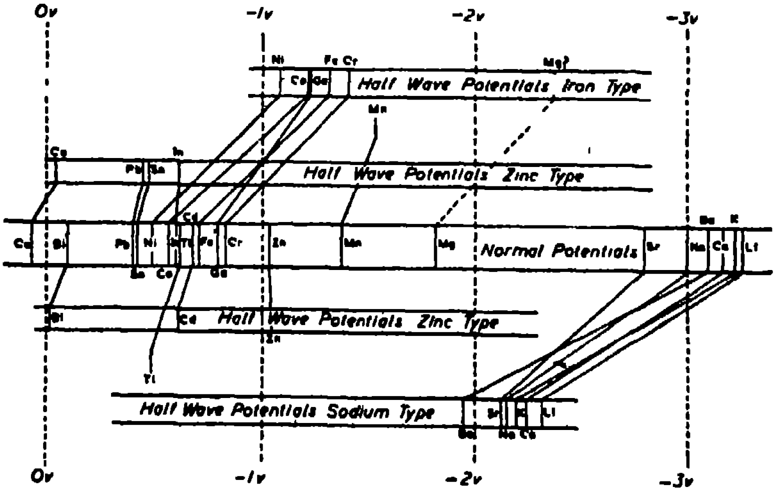
0v
-1v
-2v
-3v
Ni
Fe Cr
Mg?
Co
Cd
Half Wave Potentials Iron Type
Mn
Cu
In
Pb
Sn
Half Wave Potentials Zinc Type
Cd
Cu
Bi
Pb
Ni
Tl
Fe
Cr
Zn
Mn
Mg
Normal Potentials
Sr
Ba
K
Na
Ca
Li
Sn
Co
Ga
Bi
Cd
Half Wave Potentials Zinc Type
Zn
Tl
Half Wave Potentials Sodium Type
Sr
K
Li
Ba
Na
Ca
0v
-1v
-2v
-3v

Figure 2 Amalgam potentials

ϱ the density. The difference between this and the actual normal electrode potential gives, at least to a first approximation, a figure for calculating the true energy of amalgam formation at room temperature.

With the aid of their half wave potentials amalgams may be arranged in an electromotive series. *Figure 2* shows that the three amalgam groups already mentioned may be distinguished: the zinc amalgam type in which normal electrode potential and half wave potential are approximately the same, the iron amalgam type in which the half wave potentials are considerably more negative, and the sodium amalgam type in which they are much more positive than the normal electrode potentials.

The amalgam potentials of the zinc and sodium types are reversible, *i.e.* they are always the same whether the amalgam is not reacting, is decomposing to yield the given type of ion or is being formed by solution of the metal in mercury. This is not so for the actual potentials of the iron type amalgams. The potential on formation is considerably more negative than the resting or decomposition potentials, and this potential hysteresis is much greater than the difference between the half wave and normal electrode potentials. Thus pure iron is considerably less noble than copper and more so than zinc, but iron amalgams on formation are less noble than zinc and on decomposition more noble than copper, which corresponds to a potential hysteresis of over 1·1 v, so that iron amalgams prove much more resistant to formation or decomposition than pure iron.

Laws governing potentials and phase exchange of amalgams— The electrode potential properties of the dilute amalgams used in amalgam metallurgy can be characterized by three rules which have the general applicability of natural laws:

1 the potential of an amalgam is determined solely by its least noble component;

2 since each amalgam strives to attain a positive potential, those reactions which produce a more positive potential proceed spontaneously;

3 an amalgam is unable to take part in a reaction which does not change its potential.

The extraordinarily wide range of techniques in which amalgam metallurgy abounds depends very largely on the application of these laws. While a change in concentration of 10 per cent in a divalent metal corresponds according to Nernst's formula to an electrode potential change of scarcely 30 mv, on the other hand the different half wave potentials which normally occur are mostly separated by much more than ten times that amount, so that in consequence of *1* the potential of an amalgam is remarkably sensitive to the presence of traces of less noble impurities. Thus if lead containing 0·01 per cent zinc is dissolved in mercury, the given potential no longer resembles that of lead amalgam, but is more negative and its value is determined by the trace of zinc.

This phenomenon is also valuable since the complete removal of the smallest traces of impurities can be effected easily and quickly on account of *2*. If any solution of a lead salt is mixed with the amalgam, the traces of zinc must go from the mercury to the aqueous phase in ionic form because this makes the potential more positive, and an equivalent amount of lead ions goes from the aqueous phase to the lead amalgam, *i.e.* the phases exchange metals and this type of reaction is therefore usually called a phase exchange reaction. For example if a bismuth-tin amalgam is mixed with a bismuth-tin salt solution, it depends whether the amalgam or solution is in excess: if the former, a solution of the tin salt almost completely free from bismuth is obtained, and if the latter, a tin-free bismuth amalgam.

A consequence of *3* is that in phase exchange say in a lead-cadmium-zinc amalgam (half wave potentials −0·46, −0·63 and 1·06 v respectively against a normal calomel electrode) in contact with a lead salt solution, only zinc is exchanged for lead. Since by *1* the zinc determines the potential, exchange between cadmium and lead would not alter the potential while because of *3* it could not occur even to a minute extent so long as zinc is present in the amalgam. If the lead salt solution is not in excess and is renewed continuously, first a pure zinc salt solution is obtained, then a pure solution of cadmium salt. If, on the other hand, a solution of lead, cadmium and zinc salts is mixed with insufficient zinc amalgam, first pure lead amalgam and then pure cadmium amalgam are obtained. Thus phase exchange reactions facilitate rapid and simple preparation of both pure solutions and pure amalgams. Their power of purification and sharpness of separation exceed that of many aqueous precipitation reactions in which the precipitate frequently carries down with it foreign matter, not to mention the coarse and ineffective separation methods of traditional metallurgy.

Phase exchange goes particularly well in multicomponent salt solutions when solution and amalgam flow in counter current, *Figure 3*. The least noble metal is left in the aqueous phase while the amalgam in accordance with the dosage used in contact with the solution is connected first to the pure amalgam with the next least noble metal and finally, when a given quantity of amalgam is left for phase exchange and the rest removed, is converted to pure amalgam with the next metal in the series. The prevailing amalgam potential can serve to work an electrical relay system which adjusts through electrically operated valves the appropriate amounts of salt solution and the concentration of the aqueous phase

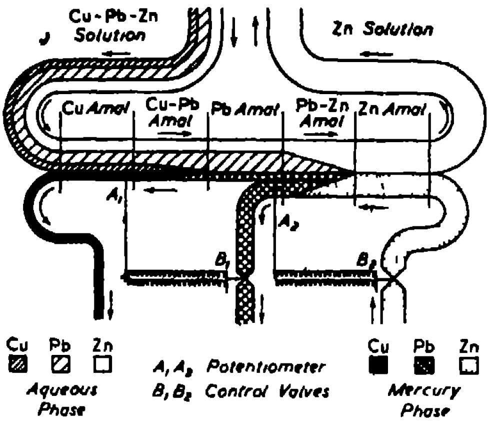

Figure 3 Automatic continuous separation of three metals by phase exchange in counter current

in contact with the amalgam. Thus a plant can be constructed which enables a multi-component salt solution to be separated automatically and continuously into its individual components.

SURFACE TENSION OF AMALGAMS

Adhesive force of mercury— Molten metals have the highest surface tension of all liquids, and where phenomena related to surface forces are found to such a marked extent these may have great technological significance. Since surface tension is known to arise from the tendency of the unsaturated forces in the atomic field to seek mutual saturation, either with atoms lying in the interior of the phase, or by foreign molecules through adsorption, mercury with a surface tension six times that of water should be an avid adsorbent with a very high adhesion, yet paradoxically in spite of its high surface tension[13] it would not appear so to the lay observer, and in fact mercury cannot wet any solid substances except a series of metals. Those with practical experience of alkali chloride electrolysis however know that it is not so easy to avoid impurities in the sodium hydroxide produced by the action of water on the sodium amalgam: the mercury which is syphoned out of the cells carries with it adsorbed sodium chloride. In amalgam metallurgical processes often operating with a rapidly circulating mercury cycle which at one point is in contact with impure solutions and then elsewhere in contact with very pure aqueous solutions (concerning amalgam metallurgical barrier electrolysis see a further article to be published on technical applications) care must be taken that these two solutions do not come into communication with each other by means of an adsorption film on the mercury surface, i.e. that they are shut off by means of an invisible flowing skin. The best method of combating this danger is by coating the barrier syphon parts with amalgam since only unamalgamated surfaces are able to carry over adsorbed films.

Surface eddies[14-16]— It has been known since about 1890 that the surface tension of mercury changes considerably with its electric potential.

According to the usual electrocapillarity curve of mercury it is a maximum at − 0·6 v (measured against a normal calomel electrode), and as the potential becomes more negative it falls steadily further below its original value. The fact that the surface tension of mercury varies with its potential has a most remarkable result: if two points in the same mercury surface have different potentials, and thus different surface tensions, the mercury will flow from the point at lower to the point at higher surface tension and the swirling of the surface is so vigorous that the mercury moves as if it had been stirred violently. Different surface tensions and the corresponding motion effects arise for instance when electrolysis takes place between electrodes which are not parallel or if the opposite electrode is too small, so producing different current loads in the mercury electrode, or if in a phase exchange reaction only part of the mercury surface is brought into the reaction. The resultant motion in the phase boundary always increases the rate of reaction so these surface forces can be used for stirring metallic systems.

Amalgam films— If an attempt is made to coat a clean iron surface, such as a polished piece of foil, with pure mercury no success is attained. If however the mercury contains a trace of sodium, amalgamation occurs at once, and the iron becomes covered with a mirror of mercury. It is clear that this is not due simply to the lower surface tension of the sodium amalgam, for pure mercury will amalgamate iron surfaces if they are in the nascent state. Thus a live iron foil cathode which is placed in an iron salt solution is immediately coated with a mercury film when a drop of mercury is put on it, and iron deposited at a mercury cathode goes immediately into the mercury phase. It is assumed that the invisible oxide layer on the iron normally prevents amalgamation; this is absent in the nascent metal and is reduced by the strongly reducing action of sodium amalgam. Zinc dust is rapidly amalgamated by sodium amalgam whereas zinc rod, but not zinc dust, is attacked by pure mercury. Iron can also be amalgamated by mercury containing a small amount of zinc if the iron surface is rubbed during the process or if it is etched with acid; probably the zinc forms an adherent layer between the iron and the mercury.

SPECIAL PROPERTIES OF AMALGAMS

Sensitiveness to oxidation— Free flowing amalgams are highly sensitive to oxidation. This is one of their most important properties and technologically is most undesirable These amalgams are so sensitive to air that even when standing they are immediately coated with a dirty grey skin, and if stirred they are soon completely converted to a mixture of metal and oxide, forming a non-flowing sludge quite useless technologically Perhaps for this reason the great advantages of amalgam metallurgy were long unrecognized, and therefore one of the most important discoveries has been that it is possible to work with amalgams in the open air, and to keep them clean and free flowing if they are covered with a solution able to dissolve the oxide of the least noble metal component of the amalgam Usually such oxide solvents, which do not attack the amalgam, can be found readily, and they are completely effective even though they are usually unable to regenerate the amalgam sludge if once it has been formed With zinc amalgam, for instance, a very dilute solution of hydrochloric acid can be used as oxide solvent, or an ammoniacal solution of an ammonium salt, for sodium amalgam even water is sufficient

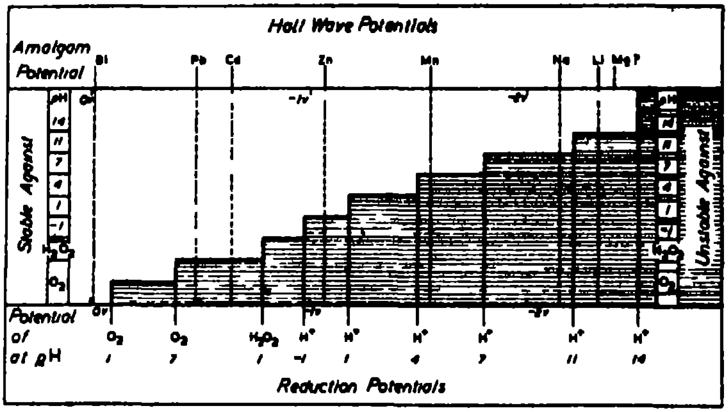

Figure 4 Stability of amalgams as a result of potential values (schematic)

Resistance to acids— The extraordinarily high resistance of amalgams to attack by strong acids arises from overvoltage shown by hydrogen ions at a mercury cathode It is interesting that the electrical deposition potential for the discharge of hydrogen ions on mercury decreases[17] by — 100 mv for each *p*H unit, so that this ion behaves as if it were semivalent If the half wave potentials of amalgams are plotted in voltage coordinates and also the reduction potentials of the hydrogen ion, of oxygen and of other oxidizing agents at different *p*H values at a mercury electrode (*Figure 4*), it is seen at once which amalgam will be attacked by a given reagent and which will not be attacked Only when the potential of the given amalgam is more negative than the relevant reduction potential has the reaction the drive necessitated by the second amalgam potential law

Mercury vaporization from liquid and solid amalgams— The thermal decomposition of amalgams and thus the removal of mercury by application of heat, takes place for zinc and sodium type amalgams as a wet distillation *i e* the mercury is boiled out of the liquid phase, while for iron type and most alloy amalgams it occurs as dry evaporation from the solid (*Schwelung*) *i e* the mercury evaporates off without the mixture being melted Similarly, ingots are left after distillation, but evaporation from the solid state yields powdered metal Corresponding to the different affinities for mercury of the three types of amalgam, the production of mercury-free metals from amalgams of the sodium type is not usually attained by simple distillation, for amalgams of the zinc type it is only possible by using relatively high temperatures, up to 900°C, whereas in the *Schwelung* process decomposed amalgams of the iron type or of alloys, the product can be obtained easily free from mercury at relatively low temperature Furthermore, with this process, the solid charge is much less corrosive than the molten metals in the distillation process, and the construction of gas tight metallic apparatus with good heat efficiency is thus not difficult Thermal preparation of amalgams suitable for the dry evaporation process is thus the usual heating procedure of amalgam metallurgy rather than distillation of the zinc and sodium type amalgams

The author wishes to thank Springer Verlag, Vienna, for permission to reproduce a diagram from a previous publication[1]

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Fluorine and Teeth

J M FLETCHER*, M A, Ph D and R H S ROBERTSON†, M A, F G S

In animal and plant life some elements, though present in small quantities, play important parts These trace elements have become familiar during the last fifty years, their discovery was made by empirical observations, but their absence has often been made good in medicine before their function was fully understood Examples are boron and manganese in the growth of healthy vegetables, cobalt in preventing pining of sheep, iodine in suppressing goitre in man, yet one important fact about trace elements is that optimal quantity and concentration often remain empirical, too little is useless, too much harmful

Since 1931, the effect of small amounts of fluorine on the appearance of teeth and on dental health has been established Due to its potential value to mankind the subject has attracted considerable research, but owing to the possibility of harmful effects from this element it is very necessary to determine the limits within which it is beneficial This article reviews the results of past surveys and research for the benefit of those who are unfamiliar with the original papers in dental and medical journals, it also discusses these results as they affect the situation in the United Kingdom

MOTTLED ENAMEL AND DENTAL FLUOROSIS

It was noted as early as 1916 that dental caries was lower in certain areas of the U S A in which unsightly brown staining of the teeth called 'mottled enamel' was endemic, but it was not until 1931 that the occurrence or absence of this mottled enamel was definitely correlated with the amount of fluoride ion in the drinking water supply[1] Later investigations have shown that in addition to brown staining fluorine is more often responsible for causing white opaque spots or streaks in the enamel Brown mottling is an extreme form of dental fluorosis which is more than likely to occur when the drinking water contains four parts per million or more of fluoride, it is also found with amounts of fluoride down to 1 p p m in communities where the standard of nutrition is particularly low In Britain it is rare, the classical example was Maldon, Essex, where the water at one time contained 5 p p m fluoride

White mottling on the other hand is of far more frequent occurrence. In its milder forms it is only readily apparent to the trained eye, and there are probably many persons in Britain who are unaware that their teeth show evidence of it Whereas it is likely to be found in districts where the water contains 1 p p m or more fluoride, surveys have discovered it in mild form in areas where there is only 0 3 p p m This concentration is high though not unusual in Britain

DENTAL CARIES

The influence of fluorine on teeth would be of minor significance were it not for its importance in reducing dental decay There have been many surveys of the relationship between dental caries and p p m fluoride in drinking water These have established that, provided other factors are constant or not widely dissimilar, there is a definite overall reduction of caries as the quantity of fluorine increases Thus from a study in 21 cities in the U S A of over 7,000 school children aged 12 to 14 years, H T Dean[2] found

Fluoride content of water supply p p m	Number of children	Affected permanent teeth per child
> 1 4	847	2 4
1 0 to 1 4	1,403	2 9
0 5 to 0 9	1,140	4 2
< 0 5	3,867	7 4

Affected teeth are classified as decayed, missing or filled teeth

These surveys have also shown that the influence of fluorine in reducing dental caries is primarily limited to its availability in the years of formation and eruption of the teeth, that is, in childhood up to the age of twelve years, subsequent availability of fluorine is of less value[3] Mottled enamel is not by itself the cause of reduced susceptibility to caries because, in areas where it is found, freedom from caries occurs to the same extent whether the teeth show mottling or not.

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In this country only one large scale survey specifically related to fluorine has so far been reported R WEAVER[4] compared the teeth of both five and twelve year old children in South Shields (with 1 4 p p m fluoride in the water) with those of North Shields (with less than 0 25 p p m fluoride) With both age groups there was 55 to 60 per cent less caries in South Shields Weaver suggests that the benefit to the children of South Shields is short lived as no significant difference was detected in the amount of caries in the adult population of the two towns. Yet in the U S A where more surveys have been made, indications of a permanent effect are found *e g* caries in army recruits aged 21 to 28 coming from high fluorine areas is significantly less than in recruits from low fluorine areas[5] On this point there is a need for further studies in this country

Availability of fluorine is by no means the only factor which influences the prevalence of caries There is an analogy between caries and the rusting of iron. Rusting requires certain conditions and involves a chain of events , it may be prevented by evolving a rustless steel, forming a protective cover on the metal, or modifying the environment in which the metal is placed In the same way decay is reduced by the structure of the teeth being good[5], by forming a protective layer by local application of a strong fluoride solution, or by avoiding oral conditions which encourage caries

Apart from traces of fluorine, good calcification of teeth results from adequate adsorption by the body of calcium and phosphorus Diets which include ample milk and vitamin D in childhood create dental conditions more capable of resisting decay The small but finite reduction in caries noted in London and other school children between 1929 and 1945 has been attributed on these grounds to the improvement in diet and provision of cod liver oil[5]

There are several factors which appear to affect caries through their influence on oral conditions Chief among these are soft foods and the inclusion of excessive amounts of sugar in the diet Many studies by the Michigan, Ohio and Californian Dental Colleges have proved the latter point[6] The fact that primitive communities such as the Eskimos, who were mainly carnivorous, have suffered a sharp increase in caries when they adopted the diets of modern civilization is largely attributable to these factors Strangely enough conditions of chronic malnutrition may also lead to immunity to caries by shifting the balance of the bacterial flora in saliva in favour of those organisms which confer natural protection Both in areas of India, and in those parts of Holland subject to ' near-starvation ' in 1945, caries has been noted as being exceptionally low Other factors are the arrangement of the teeth in the mouth, the presence of recesses not reached by saliva, personal oral hygiene, and good or bad dentistry.

Fluorine is therefore only one of several items which prevent decay and it can be overshadowed by other conditions Where nutrition is good but modern foods induce caries, local availability of fluorine has, however, lowered the rate to a significant extent in various parts of the world

AVAILABILITY OF FLUORINE

The correlation of dental health with fluorine has been established mainly from its presence as the soluble fluoride ion in drinking water In recent years improved methods of chemical analysis have enabled determinations to be made of the fluorine content[7] of foods, *Table I* With the exception of fish, particularly fish bones, and bone soups, most foods contain only traces , tea can be a rich source but does not contribute much in childhood , for an average adult diet the intake from sources other than water and tea is likely to yield 0 3 to 0 5 mg of fluorine daily This is small compared with the intake from drinking water, including that entering the diet by way of cooking, for a people such as the Americans who drink water freely, since a total daily consumption of even one pint of water with 1 p p m fluoride provides about 0 5 mg However, owing to the hot U S summer and high indoor temperature maintained there in winter, the average American child probably drinks more water than the average British child

Table I Fluorine in Common Foods

Food	*Fluorine (p p m)*	*Food*	*Fluorine (p p m)*
Milk	0 05 *to* 0 5	*Egg yolk*	0 8 *to* 1 2
Potatoes	< 0 2	*Fresh water fish*	1 6
Wheat	< 1 0	*Tinned salmon*	5 *to* 9
Oats	0 7 *to* 1 7	*Tinned sardines*	7 *to* 12
Rice	< 1 0	*Coffee (beans)*	0 2 *to* 1 6
Beef, mutton, pork	< 0 2	*Tea (leaves), various types*	10 *to* 180
Egg white	0 2 *to* 0 3	*Bone soup*	*Approx* 100

The realization that fluorine exerts its major influence in childhood has directed attention to its presence in milk , apart from the fact that the liquid intake of babies is satisfied almost entirely by milk, the encouragement given to the consumption of milk in schools has meant that a considerable proportion of the daily liquid intake of school children may now come from this fluid The fluoride content of milk varies from 0 05 up to 0 5 p p m at which level the daily consumption of 1 pint of milk supplies 0 25 mg , small though the quantity of fluorine in milk is, it has been found that it can be sufficient to cause a noticeable reduction in the amount of caries in children and adults[8].

Investigations[9] in which fluorine up to 500 p.p m was added to the drinking water of cows have shown that not more than 0 5 p p m is transmitted to the milk This observed limit to the fluorine in cows' milk conforms with that calculated from the low solubility of calcium fluoride and the calcium content of milk (1,300 p p m) The limit to the fluorine in human milk will be somewhat higher as it contains considerably less calcium (300 p p m) It is possible therefore that breast fed children of mothers who obtain fluorine either from water or from drinking certain teas will have teeth more free from decay than bottle fed children Examples of relative freedom from caries of breast fed children are known

Experiments have also been made to determine how the fluorine content of plants and food crops is changed when they are grown on soil to which fluorides have been added , there is some increase but the influence is variable and not proportional to the amount fed to the soil This point is of interest as certain rock phosphates used as fertilizers are rich in fluorine It seems that they are unlikely appreciably to affect the total fluorine intake from food by human beings, but they may have a local effect on water supplies and on cattle The information that has accumulated on the low fluorine content of food accords with the original findings that fluorine-rich drinking water is the most significant source of supply

The amount of fluorine in the water supplies of Britain has been determined for various towns and villages Some high contents of more than 1 p p m are found in certain small public and private supplies where soft water, rich in sodium salts, is taken from deep wells from strata underlying London clay A number of clays of marine origin in Southern England are also responsible for well waters with 0 3 to 1 0 p p m fluoride[10] , however, the majority of British drinking waters are low in fluorine, often with 0 1 p p m or even less, *Table II*[11] As with milk, the solubility of calcium fluoride, which is rather less soluble than calcium carbonate, places an upper limit on the fluorine content of water. Hard waters *e g.* from limestone areas, with 120 p p.m calcium are limited to about 2 5 p p m fluoride in solution, while soft waters with 12 p p m calcium can have up to three times as much.

Table II Fluorine Content of Various Water Supplies

Locality	*Parts per million*	*Locality*	*Parts per million*
Aberdeen	0 2	*Luton*	0 1
Bolton	0 4	*Mansfield*	0 5
Cardiff	nil	*Margate*	0 15
Chester	0 3	*Oxford*	nil
Edinburgh	nil	*Poole*	0 3
Glasgow (Loch Katrine)	0 1	*Preston*	0 2
Harrogate	0 6	*Salisbury*	0 22
London (Thames)	0 1	*Southampton*	0 15
London (Lea River)	0 15		
London (New River)	0 35	*Sea water*	1 15 *to* 1 30 *depending on chloride content*

FLUORINE IN THE GROWTH OF TEETH

Apart from the visible evidence of dental fluorosis revealed by mottling, the part that fluorine plays in the life cycle of teeth is largely one of conjecture. The structure of teeth at different stages of their history has been studied by various methods Use of x-rays has revealed the spatial arrangement of the prisms of which the enamel is composed[12] and has shown that the unit cells in the prisms are composed mainly of hydroxy-apatite The material between the prisms—the interprismatic substance—contains both calcium compounds, such as calcium carbonate and hydroxy-apatite, and organic matter Staining techniques show the existence of a series of channels through the enamel which make it permeable to body fluids With increasing age the channels in the permanent teeth close up Nature's problem is not easy, because not only must good communications be provided within the teeth to supply the means of calcification and to form a hard enamel, but also the enamel once formed needs to be closely compacted and of low permeability to resist decay The change from one condition to the other is not ideally rapid after eruption, so that it is at this stage, before the permeability is reduced by the slow aging process, that teeth are most susceptible to caries.

The proportion (*c* 0 1 per cent) of fluorine in enamel is very much less than it is in fluor-apatite which contains 3 9 per cent fluorine , therefore fluorine acts either by promoting good calcification or by being incorporated in a small proportion only of the enamel *e g* in the interprismatic substance, or in both ways There is evidence, such as the occurrence of dental fluorosis, that fluorine affects the calcification of teeth , on the other hand, the somewhat higher fluorine content of the enamel[13] in fluorine areas indicates that, so long as the enamel remains permeable, some of the hydroxy-apatite in it is converted to fluor-apatite This chemical change also occurs in bones which, being more porous, average a continuous rise in fluorine content from 0 05 per cent in childhood to about 0 20 per cent in old age The above picture, incomplete though it is, explains why the role of fluorine is primarily limited to childhood and permits a small secondary influence, decreasing with age, after eruption

The topical application of a strong solution of sodium fluoride, which is being tested extensively[14] on children in the U S A , appears to do little more than affect the outer layers of the enamel , yet because it reduces caries in newly erupted teeth this application emphasizes that the onset of decay is essentially a surface phenomenon

FLUORINE IN REDUCTION OF CARIES

Although there are aspects of dental decay which are not yet clear, it is no longer true to say that this disease is a mystery It arises from a chain of circumstances which may be described briefly as follows Sugars, and to a less extent starches, are the raw material for degradation to acids by bacteria in the mouth Intimate contact at places where food accumulates between carbohydrates and the dental enamel leads to attack by acids or micro-organisms, particularly where the enamel is weakened by fissures or pits , in time by slow penetration there is a breakdown of the ' brickwork ' of the enamel and a carious lesion is formed It seems probable that the existence of caries in turn promotes the growth of acid-forming bacteria such as *Lactobacillus acidophilus*, because the number of these bacilli in the saliva is proportional to the amount of caries in the mouth—a relationship which is now being used to test the efficacy of various treatments

Any circumstances which break the chain of events responsible for caries would be expected to reduce the overall incidence of this disease , the wide variety of natural conditions which affect its prevalence, and of experimental conditions by which it can be influenced, testify to the complexity of the process Although fluorine compounds are used commercially for their anti-enzymatic action, there is little evidence that the role of fluorine is to reduce, by direct action in the mouth, the growth of active bacilli Rather does its influence seem limited to opposing attack of the enamel It may do this partly by enabling the enamel to be formed with submicroscopic structure free from weaknesses and partly by increasing its resistance to mouth acids, as the solubilities of fluor-apatite and calcium carbonate are respectively lower than the solubilities of hydroxy-apatite and calcium carbonate

OTHER PHYSIOLOGICAL EFFECTS

Any recommendation to add a fluoride to food or water must ensure that no harmful effects will arise While from drinking water containing up to 4 p p m the fluorine is mainly passed out of the body through the urine, it is known that high concentrations taken internally lead to skeletal changes in humans and animals[7] Bones are as sensitive as teeth to ingested fluorine , so far there is no definite evidence that fluorine up to 4 p p m in drinking water causes any adverse effect apart from mottled enamel, but as bones, unlike enamel, can become enriched in fluorine with age, there is a need for the absence of skeletal fluorosis to be definitely proved.

Small quantities of fluorine taken internally as a fluoride salt must be distinguished from industrial fluorosis[16] which is due to hydrofluoric acid or organic fluorides in industrial smokes from the burning of cryolite, ironstone, clays, phosphates or coal This form of atmospheric pollution can be extremely harmful by causing respiratory complaints and indirectly by poisoning cattle feeding off land contaminated by it , it can also *e g* around the aluminium works at Fort William[16], lead to some dental fluorosis and a slight reduction of dental decay.

CURRENT INVESTIGATIONS

In view of the significance of caries to humanity, much research with fluorine is being carried out in the U S A The dosing of the water supply of a city by the addition of sodium fluoride is easy to accomplish at the same time as the water is chlorinated , the overall cost is small Many investigations have been started in the U S A with a fluorine level of 1 p p m[17] and from preliminary reports there is a reduction in caries of about 50 per cent The permanence of the reduction can of course only be determined after several years

Topical application by dentists is meeting with some success On the other hand fluorine added to lozenges and tablets has not been effective the small amount which can be safely incorporated and the use of insoluble rather than soluble fluorides, are probably responsible Larger amounts are possible for toothpaste and warrant extended trials

In Britain the prevalent attitude towards fluoride is one of caution This reaction may be influenced by the lack of exact knowledge of the mode of action of fluoride , however, even the most obvious adjuncts to health *e g* vitamins, are not fully understood in their modes of operation The recognition of the harmful effect of excessive fluorine in water, coming as it did before the appreciation of the beneficial effect of small quantities, strengthened the view of water engineers who maintained that their duty was to supply water in its purest form and that accessory factors should come from a well balanced diet The increasing recognition that drinking water has been a natural way of providing trace elements such as iodine as well as fluorine may now weaken this view So far no experiments with the dosing of water supply by a local authority have been initiated in Britain , certain trials such as the daily administration of 1 5 mg of sodium fluoride to children in Cheshire have been started[18] but the results are not yet reported In time much will be learnt from the U S A trials, but differences in diet, tea drinking and climate between the two countries make it desirable that we should also have first hand knowledge.

CONCLUSION

In spite of the progress made through fundamental research towards an understanding of the relation of fluorine to teeth, there still remains the need for work in Britain *a* to determine what total quantities of fluorine are likely to be consumed by babies, children and adults from water, milk, tea, soup and solid diet , *b* to determine if any harmful results to bones have resulted from the consumption of fluorine from normal diets in areas where the water contains up to 1 p p m and if so what is the critical level for fluorine , and *c* to consider the form, quantity and dilution in which fluorine could be conveniently supplied, particularly to babies and children When information on the above points has been obtained, simple methods to overcome the capricious distribution of fluorine in drinking water supplies and in the various items of the diet can be considered It may be that a background level less than 1 p p m but higher than 0 2 p p m is desirable in water In any event, there are various alternatives to the addition of a fluoride to water supplies or to administration in tablet form , the daily requirement is so small that it could easily be added to a food without affecting the taste It would seem feasible to add it for use on a regional basis to orange juice (as supplied by the Ministry of Health) or to *National* or other dried milks used by babies , or, as with iodine, it could be added to salt Also, a few drops of a 0 2 per cent solution of sodium fluoride to children's milk or drinking water

Although there are other lines of approach under investigation for the control of caries in modern civilized communities, such as a mouth-wash containing 3 per cent urea with 5 per cent diammonium phosphate[19], it appears that fluorine in limited quantities can offer a partial solution There is certainly a need for numerous practical trials which will require the willing collaboration of Health and Dental Officers with research workers

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Armour Research Foundation of Illinois Institute of Technology

H A LEEDY, A B, M S, Ph D
Director of Armour Research Foundation

ARMOUR Research Foundation of Illinois Institute of Technology is a non-profit corporation organized and operated to provide a confidential and independent research, development, and experimental engineering service to industry, government, and the general public Organized in 1936, during the worst economic depression in American history, the Foundation has grown from a staff of three scientists and an annual research turnover of $40,000 to the second largest independent research organization in the United States with a staff of 640 and an annual research turnover exceeding $4,000,000 in dollar value

Industry's recognition of science as a vital competitive aid, a method of avoiding obsolescence and a vital means of solving technological problems, is an economic phenomenon of the twentieth century The value of applied research, properly directed with its results wisely and appropriately used, is well recognized in today's highly industrialized and increasingly scientific society Many companies that support their own research laboratories have found it more economical and productive to assign certain projects to independent research organizations Through Armour and similar organizations they can rent the services of trained investigators for limited periods with specific objectives and specified budgets under strict contractual control

Moreover, they can get a new approach to their various technological problems, uninterrupted attention by research workers not harrassed by day to day production problems, and the use of a great stock of intricate and expensive equipment not available in their own laboratories and uneconomical to acquire for limited short range use

Armour Research Foundation is one of approximately 120 independent research organizations formed in various sections of the United States during the past few years Reasons for their existence and services are similar, although they vary in size, specialize in problems particular to a certain section of the country, or emphasize one field of science and engineering over others Armour's only endowment is the vast industrial strength of the United States with its many firms whose managements believe in development and progress and recognize that research is a path leading to growth and prosperity In 12 years the Foundation has served more than 2,200 sponsors as its staff has expanded and its capacity increased

The Foundation is a separate corporation with its physical facilities located at Technology Center on the near south side of Chicago Technology Center is the name given to a geographical area which includes, in addition to the Foundation, Illinois Institute of Technology, one of the nation's leading establishments in technological education and research The Foundation, the College, the affiliated Institute of Gas Technology, and the Association of American Railroads, now constructing a research laboratory, are developing a 110 acre area into one of the world's sources of higher education and fundamental and applied research The joint objective of the units at Technology Center is service to industry in and near Chicago and throughout the entire nation That these objectives are being widely recognized is evidenced by the increasing growth of Technology Center

As a public service institution devoted to applied research, the Foundation lists among its objectives those common to industrial, governmental, and public service research

> to anticipate and prevent trouble, cure existing troubles or nuisances, reduce the cost of products, increase the utility of products, reduce consumers' operating or maintenance costs develop new processes, products, or materials, improve the quality of existing materials and products, obtain better standardization, amass technical information leading to a better understanding of a product, aid national defence and promote the general welfare, develop natural resources, perform public service research, and contribute to the common store of general technological knowledge

In order to attain these objectives the Foundation maintains three major divisions Research, International, and Magnetic Recorder

RESEARCH DIVISION

The mission of the Research Division is watchful attention to the primary work of the Foundation providing high quality research This division consists of six departments, each organized into sections Small groups within each section are assigned to specific projects Supplementing the technical staff of 411 persons, who are at present working on 125 active projects, is a service group of 70 staff members whose specialities include drafting, carpentering, glassblowing, designing, instrument making, and related services

The six departments performing research are Physics, Metals, Chemistry and Chemical Engineering, Applied Mechanics, Electrical Engineering, and Ceramics and Minerals An indication of the varied types of research projects is evident from the following list of sections in each department

Physics— Light and Optics, High Pressure, Physics of Solids, Electricity and Magnetism, and Acoustics and Vibrations ,

Metals— Heat Treating and Powder Metallurgy, Non-Ferrous Metals and Welding, Ferrous Metals, Foundry Process, Abrasion, Electrochemistry, and Extraction Metallurgy ,

Chemistry and Chemical Engineering— Chemical Engineering, Physical Chemistry, Plastics, Biochemistry, Organic Chemistry, and Analytical Chemistry ,

Applied Mechanics— Structures and Materials Group, Mechanisms, Propulsion, Fluid Mechanics and Thermodynamics, Mechanics Instrumentation, a Special Analysis Group, and Engine and Lubricant Research ,

Electrical Engineering— Electrical Machines and Devices and two Electronics Sections ,

Ceramics and Minerals— Ceramics, Masonry Materials, Minerals, and Inorganic Technology

More than 110 industrial organizations and 20 government agencies sponsored research programmes at Armour in 1948, and each sponsor received direct reports and service devoted exclusively to his problems Quite often Foundation personnel conduct research in the sponsor's own plant. Industrial research projects make up the bulk of the work at the Foundation. Since many projects undertaken by the Research Division are confidential in nature or highly specialized, only a few representative projects in each of the six departments are described below

Applied Mechanics— Projects undertaken by this department for the Army Ordnance Department include the development of automatic aircraft machine guns, air-to-air rockets, improved means of artillery ammunition propulsion and investigations of interior ballistics on recoilless rifles, stresses in steel shoes of track-laying vehicles, and nozzle erosion A recent survey report on railway car designs resulted in research on a sponsored basis

Ceramics and Minerals— This department has devised a simple means of eliminating carbon dioxide from sea water which may control the deposition of scale in sea water evaporators Since Foundation research indicated that the carbon dioxide-carbonate balance affected this deposition, projected full scale tests have been planned by the U S Coast Guard Development of refractories, an adherence test for porcelain enamel, and a better scouring cleanser have been other projects of this department Attention has been aroused recently in potential markets for sodium fluosilicate A study of the chemical indicates that it may be an effective fungicide, bactericide and mineralizer

Chemistry and Chemical Engineering— In an attempt to combat turbine blade deposits, chemical engineers are searching for a metallic surface to which silicious deposits will not adhere A rapid method of drying decalcomania inks, an instrument for measuring the glossiness of tooth surfaces in the mouth by means of the ratio of specular to diffuse reflectivity, and methods of identifying lubricating oil and its location by infra-red absorption and refractivity intercept are all developments of the department

Electrical Engineering— An improved electronic blanket control and electrical specification for satisfactory copper wire connectors are typical projects in the industrial field For the Army the electrical engineers have built a mobile oscillographic laboratory, consisting of a large trailer truck housing 24 channels of recording equipment for pressure, velocity, acceleration, and time

Metals— A counter-gravity casting process, with pilot plant equipment, was worked out in the new building housing this department A magnetostrictive oscillator operating at one megacycle per second has been developed which is considered comparable to commercial quartz oscillators operating over a temperature range, and in one laboratory means of producing wire in diameters of the order of 10^{-4} in ($2\ 54 \times 10^{-4}$ cm) are being investigated Of considerable current interest is an extensive research programme directed towards the extraction and application of titanium metal

Physics— It is in this department that magnetic recording research is conducted, along with many other projects One project has been the development of multi-channel recording equipment providing for the simultaneous recording of as many as 300 pieces of information Laboratory methods for the production of imbibition colour prints have been improved, and high fidelity reproductions have found a variety of uses Noise reduction activity has included the quieting of calculating machines and a large engine development laboratory

INTERNATIONAL DIVISION

The International Division of the Foundation undertakes to provide for other countries the same impartial, non-profit, non-political industrial research available in the United States The value of this international research has been demonstrated in the creation of new sources of dollar exchange, discovery of undeveloped natural resources, selection of sound industries, encouragement of investment, training of technical personnel in various countries, and the establishment of applied research facilities

President TRUMAN's inaugural address included a reference to the technological development of other countries, a ' bold new plan ' to which United States scientists and engineers have been giving a great deal of attention Armour Research Foundation pioneered in the international field with a technological and economic survey of Argentina in 1942 Two years later, the Armour Plan was extended to Mexico with a nation-wide technological audit organized and conducted jointly by United States and Mexican technologists with headquarters in Mexico City

Laboratory research and development programmes were then started on cascalote tannin, domestic oils for leather, henequen, and other native products As projects have been completed, additional ones have been started under the continued sponsorship of the Banco de Mexico These include a new tortilla flour, survey of fluorspar resources, utilization of meat by-products, and investigations of vegetable oils In 1945 the Foundation organized the Mexican-American Conference on Industrial Research, at which mutual problems of technological development were discussed

The division was formally established in 1947, and plans for further research in Mexico and other countries, such as Haiti and Puerto Rico, are going forward A new laboratory building was completed recently in Mexico City with fully equipped laboratories, a 100 kva electric power substation, an overhead crane, a steam boiler, a variety of pilot plant equipment, technical library and offices

When full plant facilities are installed to handle the new products developed in Mexico, the value of new exports to known markets in the U S A will provide dollar exchange annually equal to 60 times the total cost since 1944 These are early results and do not take into account the contributions of training acquired by Mexican engineers

MAGNETIC RECORDER DIVISION

The third major unit of the Research Foundation is the Magnetic Recorder Division, which directs the research programme on magnetic recording, handles the commercial aspects of the licensing programme, and provides a technical service to licensees The magnetic wire recorder is one of the most valuable developments to come from the laboratories of the Foundation About 1940 a radically improved form of magnetic recording was introduced, and the resulting commercial product has made an industry

An improved magnetic powder suitable for coating paper or plastic tape, a new application of magnetic recording known as 'stereophonic' or three dimensional sound, a method of putting sound on 8 mm motion picture film easy enough for any amateur hobbyist, and improved recording heads are recent developments to come from this division At present 44 domestic companies and 12 foreign concerns are licensed to manufacture magnetic equipment patented by the Foundation Many technical articles on magnetic recording have been written by Foundation personnel and widely distributed

PUBLIC SERVICE ACTIVITIES

An example of this type of activity is the National Registry of Rare Chemicals, a widely known information service for scientists seeking rare compounds The registry has been in service for seven years and lists a total of 14,000 compounds In 1948 6,500 requests for information were received

As a public service to the citizens of Chicago, the Foundation provides a monthly analysis of dustfall at 24 sampling stations in the city

Armour cooperated in developing a standardized reproducible method of destroying red cells in blood to produce uraemia in dogs and help evaluate remedial treatment for shock, severe burns, and related disorders

The Foundation is nearing completion of early phases of one year's survey of city noises in Chicago Field studies were conducted to determine what noises may be expected at certain sites at certain times or seasons Noise in different frequency bands, and daily and annual variations of total intensity have been measured The survey has included a study of noise of various means of transport such as subway, street car, bus, and suburban trains together with comparative studies of industrial and residential areas Expected to be of world-wide use, the data may be helpful in writing city codes based on the criteria determined in the survey

The Ohmite laboratory of precision electrical measurements, a precision mechanical measurements laboratory, and an engine research laboratory for standardized engine and lubricant tests are all devoted to giving industry precise impartial information on the size or performance of their products

Several conferences and symposia on technical subjects are sponsored by the Foundation each year. A symposium on fine particles, a conference on industrial research attended by both business men and scientists, and other meetings should prove of ultimate value to the public

FOUNDATION SPONSORED PROJECTS

The maintenance of a fundamental research programme is recognized as important for the professional development of staff members and possible applications of the knowledge to future problems In 1948 the Foundation sponsored 44 such projects out of general funds of the organization High-dielectric cements, boron applications, fluid flow and heat transfer in roughened pipes, high pressure research, chemical analysis by nuclear resonance, and transients of loudspeakers have been investigated

A machine was developed which simulates service conditions involving abrasion and allows evaluations in only a few minutes instead of the months required in service This project was originally undertaken by the Foundation for subsequent industrial sponsorship Another project involved the application of moulded fibres to furniture making A resin impregnated pulp preform, made by contour felting techniques, was demonstrated in a pilot plant financed by the Foundation to have good economic and service possibilities for one-piece furniture

In any type of research in which the Foundation engages, certain criteria must be met if a project is accepted It must be in the public interest, Foundation specialists must feel that they can make a definite contribution, and the project must not conflict with others already under way

The Foundation's chief concern at all times is the ultimate value to the democratic society which supports it and in which it operates Like any self-supporting organization functioning in a free economy, the Foundation relies for its support, its growth, and its final survival upon service to and acceptance by the public

Industrial research today, properly conducted and wisely administered in the public interest, means better products, more conveniences, and greater enjoyment for all in the world of tomorrow As a progressive organization with a dynamic staff, Armour Research Foundation is helping to pave the road to a better tomorrow for all.

Miscellaneous Notes

THE ROYAL SOCIETY

OFFICERS and Council for 1950 have been elected as follows .

President	SIR ROBERT ROBINSON
Treasurer	SIR THOMAS MERTON
Secretaries	SIR EDWARD SALISBURY SIR DAVID BRUNT
Foreign Secretary	Professor E D ADRIAN

Other Members of Council— Brigadier R A BAGNOLD, Professor G L BROWN, Professor H DAVENPORT, Professor F G GREGORY, Sir CYRIL HINSHELWOOD, Professor R P LINSTEAD, Professor G F MARRIAN, Professor H S W MASSEY, Professor F E SIMON, Sir WILLIAM STANIER, Sir GEORGE THOMSON, Dr H G THORNTON, Professor C E SILLEY, Dr F M R WALSHE, Dr V B WIGGLESWORTH, Professor S ZUCKERMAN

UNIVERSITY APPOINTMENTS

Birmingham— Two new Professorships have been created in metallurgy Dr A H COTTRELL will be the first Professor of Physical Metallurgy and Dr G V RAYNOR will be the first occupant of the Chair of Metal Physics

Glasgow— The newly founded Chair of Aeronautics and Fluid Mechanics will be occupied by Professor W J DUNCAN

London— Dr S DEVONS has been appointed to the recently instituted University Chair of Physics tenable at the Imperial College of Science and Technology from 1 January

Dr W H HUGHES has been appointed to the University Readership in Bacteriology tenable at St Mary's Hospital Medical School as from 1 October 1949

At University College, the title of Reader has been conferred on the following Dr E H S BURHOP Mathematics , Dr F N DAVID Statistics , Dr L M KERBY Biochemistry , H KESTELMAN Mathematics

Sheffield— The following have been appointed to Readerships in their respective subjects Dr A S C LAWRENCE Colloid Chemistry , Dr T S STEVENS Organic Chemistry

ROYAL SOCIETY GRANT

The Council of the Royal Society has made a grant of £1,000 towards the establishment of a Great Barrier Reef Marine Biological Station probably on Heron Island This grant is being made from a fund left to the Society by the late E T BROWNE to aid marine expeditions and marine biological research

AWARDS

J Lawrence Smith Medal— The National Academy of Sciences of the United States has awarded the J Lawrence Smith Medal for Research on Meteors to Dr F L WHIPPLE, Harvard Observatory

American Chemical Society— The award in Pure Chemistry for 1949 has been made to Professor V SCHOMAKER, California Institute of Technology

INSTITUTE OF BIOLOGY

The following have agreed to join the provisional council of the proposed Institute of Biology under the Chairmanship of Dr E HINDLE Professor F ASHBY, Professor T A BENNET-CLARK, Professor G E BLACKMAN, L J F BRIMBLE, Professor J F DANIELLI, Dr D G DAVEY, Captain C DIVER, Dr J W EVANS, Professor W GRAHAM, Professor J GRAY, Professor A HADDOW, Dr J HAMMOND, Dr C HORTON-SMITH, Professor W H PEARSALL, N W PIRIE, Dr F S RUSSELL

Further particulars of the proposed Institute may be obtained from the Assistant Secretary, Dr R J C HARRIS, at the temporary offices, Chester Beatty Research Institute, Royal Cancer Hospital, Fulham Road, London, S W 3

THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

The 1950 meeting will be held in Birmingham from 30 August to 6 September The President will be Sir HAROLD HARTLEY , the General Treasurer, M G BENNETT , General Secretaries, Dr E HINDLE and Sir RICHARD SOUTHWELL .

METALLURGICAL RESEARCH COUNCIL

Professor A J MURPHY will be the new Chairman of the Inter Services Metallurgical Research Council He succeeds Professor L AITCHISON who has resigned owing to illness but who will remain on the Council

COMING EVENTS

Conference on Industrial and Safety Problems of Nuclear Technology, New York, 10–12 January

International Technical Radio Components, Accessories and Radio-electric Measuring Instruments Exhibition, Paris, 3–7 February

30th International Agricultural Machinery Exhibition, Brussels, 12–19 February

International Automobile Exhibition, Copenhagen, 24 February–19 March

Danish Industrial Exhibition, Copenhagen, 17–26 March

International Conference on the Properties of Semi-conducting Materials, Reading, 10–15 July

New Books

Metallic Creep and Creep Resistant Alloys

A H SULLY

(xii+278 pp, 138 illus, 33 tables, 8¾ in by 5½ in)

London Butterworths Scientific Publications Ltd, 1949

25s net

THE development to their present level of performance of gas turbine engines for aircraft would not have been possible without the simultaneous development of alloys capable of withstanding high stresses at high temperatures Failure under these conditions is generally a result of 'creep', that is, gradual progressive yielding under a stress that is not high enough to cause immediate fracture

The appearance of A H SULLY's book on creep is particularly timely, and will be welcomed by many who are interested in creep, whether from an engineer's point of view or because they are engaged in research on metals The author has attempted, with outstanding success, to cover the whole subject of the creep of metals Starting with an introduction in which creep is defined as 'the time dependent part of the deformation which accompanies the application of a stress to a solid', and in which the history of the subject is briefly reviewed, Dr Sully continues with a detailed discussion of the various methods of creep testing, including some specialized types

The results of characteristic creep tests are then reviewed and it is refreshing to observe that the importance of ANDRADE's classical work on the creep of metals under constant stress is recognized The vexed question of the prediction of creep properties is discussed, not only in terms of the practical study of creep but also in relation to the much more fundamental outlook developed by Andrade

A long chapter is then devoted to the theory of creep This is an up to date discussion of the current theoretical ideas on plastic deformation in which use is made when necessary of mathematical methods of expression Dr Sully observes that the theory has not yet reached the stage of predicting the behaviour of a metal or alloy from its simple physical properties, he points out that many metallurgical factors influence the creep of an alloy and discusses the effects which are significant

The remainder of the book is devoted to a description of the creep properties of a wide variety of alloys, both ferrous and non-ferrous, and to a discussion of the possibilities of a number of types of alloy that have not been developed so far This discussion, which is based on the author's wide experience in 'high temperature alloy' research, shows how the accepted generalizations might be applied to the development of new alloys

The book is excellently produced and will, without doubt, become an indispensable reference book on the subject The reviewer has only one criticism, is it necessary to follow so meticulously the practice of giving all measurements and temperatures in English and metric units ? Where exact dimensions are given, the conversions are useful, but where approximations occur perhaps it would be less irritating to the reader if the equivalents were omitted

B CHALMERS

Gmelin Handbuch der Anorganischen Chemie

Eighth edition Edited by E H E PIETSCH

No 18 Antimony,

Part B2 *(xiv+129–496 pp, 49 illus, 10 in by 6¾ in)*

Part B3 *(xxi+xvi+497-564 pp, 4 illus)*

No 68 Platinum, Part A5 *(vii + 533-718 pp, 61 illus)*

Clausthal-Zellerfeld Gmelin Verlag G m b H 1949

DM 83 60, 24 75 and 43 00 respectively

THE editor and staff of Gmelin are to be congratulated on the appearance of three further volumes The first completes the account of the physical and electrochemical properties of antimony, deals in detail with its detection and estimation and covers in part the chemistry of antimony compounds The latter include those with hydrogen, oxygen, nitrogen and the halogens In the second volume antimony compounds with sulphur and other non-metallic elements are described The third volume is more specialized and deals with the alloys formed by ruthenium, rhodium and palladium

It is difficult to overstate the value of this work to chemists throughout the world Its reputation for completeness and accuracy and, above all, for a critical assessment of facts and data has always been high That this standard should have been fully maintained in post war volumes produced under difficulties of all kinds merits the highest praise Such an achievement would be possible only when each branch of the subject is dealt with by a group of experts impelled by a sense of devotion to their task There are many who believe that in the years ahead inorganic chemistry will become more and more closely associated with physical chemistry and that, together, the two subjects will increase greatly in importance This handbook emphasizes the need for such a marriage of the two branches of chemistry for in its pages physics, physical chemistry and purely descriptive inorganic chemistry have equal places Many volumes remain to be published and will be eagerly awaited It is to be hoped that this task may be completed rapidly, at least as far as the chief outstanding elements are concerned, and that increased sales may make possible a reduction in the rather high selling price

H. J EMELÉUS

Lighting Technique

B F FEDOROV

Translated from the Russian by W R STOKER *with additional sections on fluorescent lighting by* W T O'DEA

(300 pp, 128 illus, 8½ in by 5½ in)

London Hutchinson's Scientific and Technical Publications, 1949 25s net

THIS is a translation of a Russian textbook for engineering students It sets out to teach the fundamentals of the subject, and in some respects it is successful , the student who follows the chapters on fundamental concepts, light sources and methods of calculation, particularly if he works out the examples, will have acquired a facility in manipulating the quantities used in illuminating engineering The book suffers, however, in its academic approach , the reader can hardly escape the impression that the authors are more at home in the classroom than in the practice of lighting The translator is evidently unacquainted with the practice of illuminating engineering, with the result that he uses unfamiliar expressions where well established English terms exist, which is irritating and sometimes confusing Something more than an understanding of the language is needed to make a good translation, and the translator has evidently experienced the difficulty of escaping from the net of foreign constructions which have brought him to such phrases as ' This kind of lighting is quite impermissible whatever the value of illumination is set up ' The reader familiar with British terminology would probably be puzzled by ' angular coefficients ' and ' reserve factor ' and would be confused by such statements as ' The *light efficiency* is the ratio of the luminous flux expressed in light watts to the total radiant flux of the radiation expressed in watts ' and ' The *luminous output* is the ratio of the luminous flux expressed in lumens to the total radiant flux of the radiation expressed in watts ' —particularly as the term ' light efficiency ' is used frequently a few pages later to mean something else The book is so confined to Russian practice and thought that its value outside Russia is limited

The discussion of units and quantities and methods of calculation is, however, thorough and consistent, which in the confusion of illumination quantities is something of an achievement Metric quantities are used throughout The author starts logically with luminous flux as the basic quantity , and in his discussion of the calculation of illumination he uses some elegant theorems not often given in textbooks Reference to the Isocandle diagram is curiously omitted The section on ' The Lighting of Rooms and Workplaces ' is mainly concerned with the Soviet regulations for illumination, mounting height and so forth and the calculations involved The author is unfamiliar with other recommendations, and the levels recommended are low by our standards The section on outdoor lighting deals with lighting of outdoor workplaces, railway yards, substations, streets and squares, giving the Russian official recommendations A tremendous formula is given for calculating the height of projectors in railway yard lighting which is incomprehensible as printed , but in the next paragraph it is explained that standard heights are used Street lighting is treated on the basis of illumination A chapter on A R P lighting completes the text

The series of 18 pages of exercises which follow is to be commended, and the student who works through them conscientiously will find that they clarify the text considerably Tables of data are given, of varied usefulness , appendix 9 giving the theoretical basis of utilization coefficients, 11 pages long, would have been much more useful if given in the more usual form, and the student will probably use appendix 10 for quick reference rather than work out utilization coefficients in detail Appendix 4 gives details of some popular Russian lighting fittings, but the polar curves shown bear little relation to the form of the fitting or to the tabulated values in appendix 5

W T O'DEA contributes some short sections on discharge and fluorescent lamps and their use

There are no photographic illustrations , the bibliography contains nine references, seven of which are Russian and the other two, both American, are dated 1934 and 1936 respectively There are no references to papers, which is a pity, since the book makes some interesting ascriptions such as the first arc lamp to PETROV (1802), six years before DAVY, and the filament lamp to GOEBEL (1854), which it would be interesting to verify Several misprints occur , particularly in the mathematics, which would be improved if symbols were printed in italics

J M WALDRAM

Citrus Products Chemical Composition and Chemical Technology

J B S BRAVERMAN

(xiv+424 pp, 106 illus, 9½ in by 6 in)

New York Interscience Publishers Inc , 1949 $9 00
London Interscience Publishers Ltd, 1949 72s

AN interesting book, bringing up to date the newer knowledge of the citrus industry, an industry of increasing importance to the economy of various parts of the world and particularly perhaps to Israel The sub-title includes ' Chemical Composition ', and it appears that the author has been at pains to cull from the chemical literature some of the latest theories on the structure of the various entities found in citrus fruits These dissertations, which occupy some 166 of the 400 pages of the book, do not appear to be integral to the subject and would only be of value to students denied a wider source of study and of reference

It is not necessary to detail the various chapters nor to define the scope for, from the technological angle, the work is very full and covers every phase of the industry, and covers it very adequately Moreover, the author has succeeded in including the newer knowledge

A full bibliography adds to the value of the book, which is well printed and free from gross errors, although there are some examples of looseness of expression *e g* a refractometer does not measure *total* solids but *soluble* solids

It is a useful book to anyone interested in the technology of citrus products

L H LAMPITT

Books to Come

Bestimmte Integrale W GROBNER and N HOFREITER (*30 × 21 cm*) Vienna Springer Verlag

Structure of Molecules Y K SYRKIN and M E DYATKINA *Translated and partly revised by* D O JORDAN and M A PARTRIDGE (*c 560 pp, c 80 illus, royal 8vo*) London Butterworths Scientific Publications Ltd *c 52s 6d*

Technique of Organic Chemistry, Vol I *Edited by* A WEISSBERGER Part I (*1,084 pp, 395 illus, 93 tables, 9 in by 6 in*) Part II (*1,041 pp, 355 illus 64 tables*) New York and London Interscience Publishers Inc *$18 50* or *£5* each

Genes, Plants and People C D DARLINGTON and K MATHER (*illus, demy 8vo*) London George Allen and Unwin Ltd *c 7s 6d* net

Elements of Internal Combustion Turbine Theory. H T ADAMS (*xii + 178 pp, 183 illus, 3 charts, demy 8vo*) London Cambridge University Press *16s* net

Zahlentheorie H HASSE (*xii + 470 pp*) Leipzig: Akademie Verlag *DM 44 00*

Gesammelte mathematische Abhandlungen von Ludwig Schläfli (1814–1895) I (*390 pp*) Basel Verlag Birkhäuser *S Fr 44 00*

Radiative Transfer S CHANDRASEKHAR (*400 pp, 35 illus, royal 8vo*) Oxford Clarendon Press *c 35s* net

Forum: Defence Services Research Facilities

IN many fields of scientific work the Defence Services possess equipment, knowledge and personnel which, if available, might be used to help scientific researches unconnected with any Service objective In some cases facilities of this kind have been provided for several years In 1948 the Defence Services Research Facilities Committee was set up by the Royal Society, not, as some have supposed, to offer scientific help to the Services but to enlist the help of the Services on behalf of scientific workers The terms of reference of the Committee are

To consider proposals for the use of Service facilities and personnel for assisting scientific research and to make recommendations to the Council of the Royal Society, the Lords Commissioners of the Admiralty, the Army Council, the Air Council and the Minister of Supply

To give an idea of the facilities which the Committee hoped would be available, the subjects dealt with by the five panels which were established to consider applications for help are listed below

Panel	A	Submarine Gravity Measurements
,,	B	Surplus Explosives
,,	C	Magnetic Survey
,,	D	Aerial Photography
,,	E	Scientific Expeditions

The Defence Services have been most cooperative The following instances illustrate the scope of the help which they have already given

The Admiralty provided a submarine on two occasions for gravity observations at sea

Two flights were made in Sunderland flying boats of Coastal Command to observe the breeding grounds of seals and seabirds

The cooperation of the Ministry of Supply was obtained in the development of an airborne magnetometer

The War Office lent equipment to a geological expedition to Spitzbergen

The Air Ministry provided a helicopter fitted with a large net for collecting insects

The Admiralty agreed to lend a kite balloon and personnel for research on the feeding habits of swifts

The Air Ministry agreed to provide photographic cover for an archaeological expedition to Tripolitania.

Arrangements were made for the R A F to fly photographic plates at high altitudes in connection with cosmic ray research

The International Committee for Bird Preservation borrowed from the Air Ministry six cameras for use in a wildfowl census

The Air Ministry has supplied a considerable number of aerial photographs of specific areas required by scientists from time to time

Scientists wishing to submit proposals for consideration by the Committee should communicate their suggestions in the first instance to the Assistant Secretary of the Royal Society, Burlington House, London, W 1

G I TAYLOR

Royal Society Chairman of the Defence Services
Burlington House Research Facilities Committee of
London, W 1 the Royal Society

Use of Inequalities in Polymer Research

G HERDAN, D I C , M Sc , Ph D

The differences between molecular weight averages of polymers obtained by different methods of determination are interpreted in terms of inequalities, and the relationship between these inequalities and the degree of polydispersity is shown This leads to identification of three important empirical relations between such averages as three fundamental algebraic inequalities (first section) It is shown how to calculate directly, without any assumptions about the distribution law, the standard deviation, and the higher characteristic parameters, of the distribution of molecular weights from a knowledge of averages of different order by utilizing certain relations between them Knowing the mean and the standard deviation, we are in a position to estimate the general outline of the distribution curve by applying a certain statistical inequality (second section) In order to obtain a 'best fitting' curve to the distribution of macromolecules, without assumptions about the law governing such distributions, use is made of inequalities between certain parameters which characterize the polydisperse substance and those which would obtain from a normal distribution (third section) Numerical illustrations are given for all methods developed in the paper

INEQUALITIES BETWEEN AVERAGES AND THEIR RELATION TO POLYDISPERSITY

THE molecular weight of a polymer as obtained by one or another method of determination is an average molecular weight, the structure of which differs according to the method of determination[1] What follows is a short survey of the types of averages arising in polymer investigations, and of the relationships subsisting between them

Notation— Let M_i stand for the molecular weight of the molecular species i, and n_i for the number of molecules of weight M_i, furthermore, let

$\Sigma n_i = N$ the total number of molecules in the sample

$n_i M_i = g_i$ the weight of the species M_i

$\Sigma n_i M_i = G$ the total weight of the sample

$g_i/G = \gamma_i$ the weight fraction of M_i

$\Sigma \gamma_i = 1$

The distribution of the total number of molecules with regard to molecular weight M_i is called the Number distribution, and that of the total weight with regard to molecular weight M_i the Weight distribution Their respective arithmetic means are

Number average $M_n = \Sigma M_i n_i/N$

Weight average $M_w = \Sigma M_i g_i/G = \Sigma M_i^2 n_i/\Sigma M_i n_i$

The arithmetic mean is often described as the first moment of the distribution about zero and, as such, is the first in the series of moments which characterize the distribution It is thus only a special class of average *viz* the average of M_i to the first power Instead, we may have

Number distribution	Weight distribution
${}_n\mu'_1 = {}_n a_1 = \dfrac{\Sigma M_i n_i}{N} = M_n$	${}_w\mu'_1 = {}_w a_1 = \dfrac{\Sigma M_i g_i}{G} = M_w$
${}_n\mu'_2 = {}_n a_2^2 = \dfrac{\Sigma M_i^2 n_i}{N}$	${}_w\mu'_2 = {}_w a_2^2 = \dfrac{\Sigma M_i^2 g_i}{G}$
${}_n\mu'_3 = {}_n a_3^3 = \dfrac{\Sigma M_i^3 n_i}{N}$	${}_w\mu'_3 = {}_w a_3^3 = \dfrac{\Sigma M_i^3 g_i}{G}$

and, generally*,

$$ {}_n\mu'_r = {}_n a_r^r = \frac{\Sigma M_i^r n_i}{N} \qquad {}_w\mu'_r = {}_w a_r^r = \frac{\Sigma M_i^r g_i}{G} $$

where μ'_1, μ'_2, μ'_3, μ'_r are called statistical moments of the variable M_i about the origin, μ'_1 being the first, μ'_2 the second, μ'_r the rth moment. To each moment belongs an 'average' of corresponding order a_r, being the rth root of the rth moment

If, instead of the absolute value M_i of the variable, the deviations m_i from the arithmetic mean are used in the above formulae, then

$$ {}_n\mu_1 = \frac{\Sigma m_i n_i}{N} \qquad {}_w\mu_1 = \frac{\Sigma m_i g_i}{G} $$

$$ {}_n\mu_2 = \frac{\Sigma m_i^2 n_i}{N} \qquad {}_w\mu_2 = \frac{\Sigma m_i^2 g_i}{G} $$

$$ {}_n\mu_r = \frac{\Sigma m_i^r n_i}{N} \qquad {}_w\mu_r = \frac{\Sigma m_i^r g_i}{G} $$

represent the first, second rth moment about the mean

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* The quantities μ_r, a_r will be written without the left hand subscript where there is no risk of confusion

The second moment about the mean is of special interest, since it represents the standard measure for dispersion To obtain it, the square of the arithmetic mean is subtracted from the second moment about zero, the result being the squared Standard Deviation

$$\begin{array}{ll} \text{Number distribution} & \sigma_n^2 = {}_n\mu'_2 - M_n^2 \\ \text{Weight distribution} & \sigma_w^2 = {}_w\mu'_2 - M_w^2 \end{array} \qquad (1)$$

As regards the relationships between moments of different order, it can be shown that

$${}_na_1 \leqslant {}_na_2 \leqslant {}_na_3 \qquad \text{and} \qquad {}_wa_1 \leqslant {}_wa_2 \leqslant {}_wa_3$$

and, generally, that the *r*th root of the *r*th moment about zero is equal or greater than the $(r-1)$th root of the $(r-1)$th moment about zero, for all *r*'s[3] These inequalities become equalities when all the values of the variable are equal The more, on the other hand, the measurements deviate among themselves, the greater will the inequality be It may, therefore, serve as a measure of polydispersity

The average molecular weight

$$M_w = \Sigma M_i g_i / G = \Sigma M_i^2 n_i / \Sigma M_i n_i$$

appears to be the ratio of two moments (averages) of the number distribution *viz* ${}_na_2^2/{}_na_1$ Similarly, the *z* average

$$M_z = \Sigma M_i^2 g_i / \Sigma M_i g_i = \Sigma M_i^3 n_i / \Sigma M_i^2 n_i$$

appears to be the ratio of two moments (averages) of the weight distribution ${}_wa_2^2/{}_wa_1$ or of the number distribution ${}_na_3^3/{}_na_2^2$ This applies to all the higher order averages M_{z+1}, M_{z+2} *etc*

As is well known, the ratios M_w/M_n, M_z/M_w afford a measure of the degree of polydispersity[3, 4] Written explicitly as

$$\frac{M_w}{M_n} = \frac{\Sigma M_i^2 n_i \; \Sigma n_i}{(\Sigma M_i n_i)^2} \quad \text{and} \quad \frac{M_z}{M_w} = \frac{\Sigma M_i^2 g_i \; \Sigma g_i}{(\Sigma M_i g_i)^2}$$

they are recognized as special cases of the Cauchy inequality[5]

$$\Big(\sum_1^n a_i b_i\Big)^2 \leqslant \sum_1^n a_i^2 \sum_1^n b_i^2 \qquad (2)$$

with

$$a_i = M_i / n_i^{\frac{1}{2}}, \quad b_i = n_i^{\frac{1}{2}}$$

for the number, and $a_i = M_i g_i^{\frac{1}{2}}$, $b_i = g_i$ for the weight distribution In its integral form

$$\frac{\int y^2 \, dx \int dx}{\left(\int y \, dx\right)^2} \geqslant 1$$

this inequality is often referred to as the Schwarz inequality[6]

It is because the ratios between the molecular weight averages conform to the Cauchy inequality that they afford measures of the polydispersity This then is the theoretical basis of the empirical finding of $M_n \leqslant M_w \leqslant M_z$ in the case of polydispersity Again, these inequalities become equalities when all the values of the variable are the same *e g* if the substance were homogeneous with regard to molecular size On the other hand, it becomes more marked as the diversity increases

Since the best quantitative measure for polydispersity is the standard deviation, it would be of great value to know the relation between the Cauchy inequality M_w/M_n or M_z/M_w and the standard deviation This can be done without any assumption as to the form of the distribution curve, as shown for equations 9a, 9b where we obtain

$\sigma_n = (M_w M_n - M_n^2)^{\frac{1}{2}}$ for the number distribution and
$\sigma_w = (M_z M_w - M_w^2)^{\frac{1}{2}}$ for the weight distribution

The higher terms in the expression for Hc/τ according to Debye's formula for the dependence of the molecular weight of a polymer upon the turbidity of a polymer solution[7, 8] contain the quantities

$$\frac{\Sigma M_i^2 \gamma_i}{(\Sigma M_i \gamma_i)^2} \quad \text{and} \quad \frac{\Sigma M_i^3 \gamma_i}{(\Sigma M_i \gamma_i)^3}$$

Writing them as

$$\frac{\Sigma M_i^2 \gamma_i}{(\Sigma M_i \gamma_i)^2} = \frac{\Sigma M_i^2 g_i (\Sigma g_i)^2}{(\Sigma M_i g_i)^2 \Sigma g_i} = \frac{\Sigma M_i^2 g_i \; \Sigma g_i}{(\Sigma M_i g_i)^2}$$

and

$$\frac{\Sigma M_i^3 \gamma_i}{(\Sigma M_i \gamma_i)^3} = \frac{\Sigma M_i^3 g_i (\Sigma g_i)^3}{(\Sigma M_i g_i)^3 \; \Sigma g_i} = \frac{\Sigma M_i^3 g_i (\Sigma g_i)^2}{(\Sigma M_i g_i)^3} \qquad (3)$$

the first is recognized as a special case of the Cauchy inequality and the second as an example of the more general Hölder inequality[9]

$$\sum_1^n a_i b_i \leqslant \Big(\sum_1^n a_i^r\Big)^{1/r} \Big(\sum_1^n b_i^{r'}\Big)^{1/r'} \qquad (4)$$

for $r > 1$ and $1/r + 1/r' = 1$ with $a_i = M_i g_i^{1/3}$, $b_i = g_i^{2/3}$, $r = 3$, $r' = 3/2$ This applies similarly to the higher terms in the expression for Hc/τ

The relation between this inequality for $r > 2$ and the standard deviation of the weight distribution of molecular weights σ_w is given[10] by

$$\frac{\Sigma M_i^r \gamma_i}{(\Sigma M_i \gamma_i)^r} \geqslant (1 + \sigma_w^2 / M_w^2)^{r-1} \qquad (5)$$

Therefore

$$\sigma_w^2 \leqslant \frac{(\Sigma M_i^r \gamma_i)^{1/(r-1)}}{(\Sigma M_i \gamma_i)^{r/(r-1)}} M_w^2 - M_w^2$$

Writing μ'_r for the *r*th moment of the weight distribution $\Sigma M_i^r \gamma_i$, the inequality can be expressed as

$$\sigma_w^2 \leqslant \frac{\mu_r'^{1/(r-1)}}{\mu_1'^{r/(r-1)}} \mu_1'^2 - \mu_1'^2$$

or

$$\sigma_w^2 \leqslant \mu_r'^{1/(r-1)} \, \mu_1'^{(r-3)/(r-1)} - \mu_1'^2 \qquad . \quad (6)$$

This is the generalization of the expression for the equality $\sigma_w^2 = M_z M_w - M_w^2$, given above Similarly for the number and z distributions

In Svedberg's formula for the molecular weight

$$M_i = \text{const } s_i/D_i$$

M_i appears as a function of the sedimentation and diffusion constants s_i and D_i Since s_i and D_i differ from one molecular species to another depending, as they do, upon the size of the macromolecules and since the molecular weight of a polymer is an average molecular weight, M could be calculated as being proportional to the average of all the ratios s_i/D_i, say (s_i/D_i), in the polymer But the actual mathematical procedure is different the averages s and D are substituted in the above formula and the average molecular weight M is calculated, not as being proportional to the average of the ratio s_i/D_i, but to the ratio of the two averages s/D

Remembering now that s_i and D_i themselves may be averaged in different ways, yielding either the number, weight or z averages, to name only these three types, and may thus enter the formula as s_n, s_w, s_z and D_n, D_w, D_z, it is clear that M will be neither a pure number, weight, nor z average, but proportional to the ratio of any two such averages As symbol for this type of composite average, we use M_{jk} where $j = n, w, z, z+1$ and $k = n, w, z, z+1$ Thus if the ratio of averages is s_w/D_w the molecular weight average will be M_{ww} and if s_n/D_z, it will be M_n These composite averages are not, as a rule, equal to the simple averages Their difference stands in a definite relationship to the dispersion of molecular species in the polymer

The inequality between M_j and M_{jk} is of a different type to those encountered hitherto It can be expressed[10] as

$$|s/D - s/D| \leqslant (K\sigma_D^2 + \sigma_s\sigma_D)/D^2 \qquad (7)$$

where K is the maximum ratio s_i/D_i, and σ_s, σ_D represent the standard deviations of s_i and D_i respectively

In order to show the dependence of the inequality upon the properties of the distributions of s_i and D_i more clearly, we write v_D for σ_D/D and the right hand side becomes

$$(K\sigma_D^2 + \sigma_s\sigma_D)/\bar{D}^2 = Kv_D^2 + (\sigma_s/\sigma_D)v_D^2 = v_D^2(K + \sigma_s/\sigma_D)$$

and

$$|s/D - s/\bar{D}|/v_D^2 - K \leqslant \sigma_s/\sigma_D$$

Substituting now for s/D the symbol M_j/C, and for s/D the symbol M_{jk}/C, where C is constant, we have

$$|M_j - M_{jk}|/C\, v_D^2 - K \leqslant \sigma_s/\sigma_D \qquad (8)$$

from which we see that on the basis of the inequality between M_j and M_{jk} conclusions may be drawn as to the ratio between the two standard deviations σ_s and σ_D This gives the general structure of the relationship which JULLANDER[4] has treated for the log normal law governing both the s_i and D_i distributions

ESTIMATING THE POLYMER DISTRIBUTION BY MEANS OF STATISTICAL INEQUALITIES

The log normal law—It is sometimes assumed that the distribution of molecular weights is governed by one or another form of the so-called log normal law[3, 4, 11] If the simple log normal law is assumed, then $a_2/a_1 = a_3/a_2 = \ldots a_r/a_{r-1} = \exp\{\tfrac{1}{2}(\ln\sigma_g)^2\}$ where $\ln\sigma_g$ is the natural logarithm of the geometric standard deviation, which is equal to the standard deviation of the logarithmic distribution In terms of the averages M_n, M_w, M_z we have for this distribution

$$M_w/M_n = M_z/M_w \qquad M_r/M_{r-1} = \exp(\ln\sigma_g)^2$$

This establishes the relationship between averages of different order and the standard deviation, but only for the simple log normal distribution That polymer data are not too well fitted by it may be seen from the fact that the criterion $M_z/M_w = M_w/M_n$ does not generally hold[4, 14] Furthermore, it has only descriptive value, since there is no ground for assuming that the mechanism of polymerization is the same in all polymers and governed by the same logarithmic law

Calculation of the standard deviation without assuming the log normal law—It has so far escaped observation that from a knowledge of M_w and M_n the standard deviation of molecular weights can be calculated directly and exactly without any assumption whatsoever about the distribution law Since this article was written ROBERTSON has drawn my attention to a paper of his[17] in which that relation was derived

The standard deviation of the number distribution is given by (see p 36)

$$\sigma_n = ({}_n\mu'_2 - M_n^2)^{\frac{1}{2}}$$

and since the product

$$M_w M_n = \frac{\Sigma M_i^2 n_i\ \Sigma M_i n_i}{\Sigma n_i\ \Sigma M_i n_i} = \frac{\Sigma M_i^2 n_i}{\Sigma n_i} = {}_n\mu'_2$$

we have

$$\sigma_n = (M_w M_n - M_n^2)^{\frac{1}{2}} \qquad (9a)$$

Similarly, the standard deviation of the weight distribution is

$$\sigma_w = ({}_w\mu'_2 - M_w^2)^{\frac{1}{2}}$$

and since the product

$$M_z M_w = \frac{\Sigma M_i^2 g_i\ \Sigma M_i g_i}{\Sigma g_i\ \Sigma M_i g_i} = \frac{\Sigma M_i^2 g_i}{\Sigma g_i} = {}_w\mu'_2$$

we have

$$\sigma_w = (M_z M_w - M_w^2)^{\frac{1}{2}} \qquad (9b)$$

Illustration—For a sample of polystyrene the following averages were determined[11]

$$M_n = 146\,000 \qquad M_z = 464\,000$$
$$M_w = 280{,}000 \qquad M_{z+1} = 705{,}000$$

From formula 9a we obtain the standard deviation of the number distribution as $\sigma_n = 144{,}500$, and from formula 9b the standard deviation of the weight distribution as $\sigma_w = 224{,}900$. The skewness of the weight distribution calculated according to the formula μ_3/σ^3 is 2.324, which implies considerable asymmetry.

The Tchebycheff inequality—Knowing the mean and the standard deviation in either number or weight distribution of molecular weights, we can obtain a conservative estimate of the whole distribution by using the so-called Tchebycheff inequality[12]. According to this, the proportion of molecules with molecular weights differing from the mean by an amount not exceeding $\pm\, t$ times the standard deviation is, at least, $1 - 1/t^2$ and, therefore, the proportion of molecules with weights differing from the mean by more than $\pm\, t$ times the standard deviation is, at the most, $1/t^2$.

In particular, the proportion of observations (molecular weights) deviating from the arithmetic mean by more than

$\pm\, 2\sigma$ is equal to or less than $1/4$
$\pm\, 3\sigma$,, ,, ,, ,, ,, ,, $1/9$
$\pm\, 4\sigma$,, ,, ,, ,, ,, ,, $1/16$

$\pm\, t\sigma$,, ,, ,, ,, ,, ,, $1/t^2$

Conversely, the probability W for an observation to deviate from the arithmetic mean by an amount not exceeding $\pm\, t$ times the standard deviation is at least equal to

$$W \geqslant 1 - 1/t^2 \qquad (10)$$

It is evident that this relationship is of use only for $t > 1$.

The estimate is a very conservative one, since the actual value of W is usually much more than $(1 - 1/t^2)$. Under certain conditions an improvement is possible. If the distribution is continuous, unimodal and with skewness as measured by (Mean − Mode)/σ of less than unity, then the inequality can be improved to

$$W \geqslant 1 - 1/2.25\, t^2 \qquad (11)$$

which is known as the Camp-Meidell inequality.

Illustration—Let us suppose a certain polymer gave a number average $M_n = 15{,}000$ and a weight average $M_w = 20{,}000$. According to formula 9a the standard deviation of the number distribution is then calculated as

$$\sigma = (M_w M_n - M_n^2)^{\frac{1}{2}}$$
$$= \{(300 \times 10^6) - (225 \times 10^6)\}^{\frac{1}{2}}$$
$$= 8{,}660$$

From formula 10 it follows that for, say

$t = 1.5,\quad W \geqslant 56$ per cent
$t = 2.0,\quad W \geqslant 75$ per cent
$t = 2.5,\quad W \geqslant 84$ per cent
$t = 3.0,\quad W \geqslant 89$ per cent
$t = 3.5,\quad W \geqslant 92$ per cent
$t = 4.0,\quad W \geqslant 94$ per cent

and, therefore, the percentage of molecules with weight deviating from M_n by an amount not exceeding 1.5σ i.e. molecules having weights between 15,000 and 15,000 ± 12,990, will be at least 56 per cent, the percentage of molecules with weights deviating from M_n by an amount not exceeding 2.0σ i.e. molecules having weights between 15,000 ± 17,320 will be at least 75 per cent, and so on.

Making the steps between the multiples t of σ small (perhaps 0.1) and subtracting the percentage of molecules for each such multiple from that for the next higher multiple, the fractions of molecules with weights between narrow limits (according to the magnitude of the steps) are obtained and the whole distribution curve can thus be reconstructed.

If there is considerable asymmetry, construction of the distribution curve becomes difficult since, without further experimental data we do not know what proportion of these percentages lies to the right, and what proportion lies to the left of the mean. This difficulty is overcome by using the generalization of the Tchebycheff inequality known as the Markoff inequality[14].

Furthermore, since the Markoff inequality can be applied whenever it is either impossible or inconvenient to obtain the basic information for the use of the Tchebycheff inequality, it represents a useful tool for the investigation of polydispersity[15].

THE BRUNS' SERIES AS A MEANS FOR CALCULATING THE DISTRIBUTION OF MOLECULAR WEIGHTS

The inequalities which we shall employ here are the points of departure of the distribution in question from normality. They are epitomized by the inequalities between the moments (or functions of moments) of the given polydisperse substance and those which would obtain from a normal distribution with the same mean and standard deviation.

The Bruns' series is the expansion of the difference or inequality between the cumulative percentage $W'(x)$ of the given distribution and the corresponding percentage $N(x)$ of the Gaussian curve in an infinite series which, like that of Fourier, progresses according to certain basic functions[16] Its terms are the products of a coefficient and the successive derivations of the normal or Gaussian curve

$$W'(x) = \mathcal{N}(x) + c_0\varphi(x) + c_1\varphi'(x) + c_2\varphi''(x) + \qquad (12a)$$

where, in the usual notation,

$$\mathcal{N}(x) = \Phi(x) = \tfrac{1}{2}\,[\theta(x) + 1]\,\frac{1}{\pi^{\frac{1}{2}}}\int_0^x \exp(-x^2)dx + \tfrac{1}{2}$$

$$\varphi(x) = \frac{1}{\pi^{\frac{1}{2}}}\exp(-x^2)$$

$$x = (X - \bar{X})/1{\cdot}414\sigma$$

and $\varphi'(x)$, $\varphi''(x)$, $\varphi'''(x)$ are the successive differential coefficients of $\varphi(x)$

Generally, we have

$$\varphi^{(r)}(x) = \varphi(x)p_r(x)$$

where $p_r(x)$ are the Hermite polynomials

The Bruns' series thus becomes

$$W'(x) = \Phi(x) + 1/\pi^{\frac{1}{2}}\exp(-x^2)[c_0p_0(x) + c_1p_1(x) + \quad] \qquad (12b)$$

The coefficients are calculated so as to make the difference between the norm and the approximation a minimum and, for the standardized variable $x = (X - \bar{X})/1{\cdot}414\sigma$, result as

$$\begin{aligned} c_0 &= 0 \\ c_1 &= 0 \\ c_2 &= 1/3!\,(2)^{3/2}\,(-\mu_3/\sigma^3) \\ c_3 &= 1/4!\,(2)^{4/2}\,(\mu_4/\sigma^4 - 3) \\ c_4 &= 1/5!\,(2)^{5/2}\,(-\mu_5/\sigma^5 + 10\mu_3/\sigma^3) \\ c_5 &= 1/6!\,(2)^{6/2}\,(\mu_6/\sigma^6 - 15\mu_4/\sigma^4 + 30) \end{aligned} \qquad (13)$$

where the μ_r are the moments about the mean

For working with the Bruns' series in polymer research, the following graphical version has been developed so as to reduce arithmetical labour to a minimum

According to the 'normal development' of the cumulative or integral series (equation 12b), the cumulative frequency at any point can be expressed by a value of the probability integral (the error function) plus a correction term

The value of the probability integral for specified multiples of σ can be read off numerical tables for that function, but we shall use its graphical representation in the form of probability graph paper where the ordinate is the Gaussian probability integral $\Phi(x)$ and the abscissa is the standardized variable *i e* the variable in terms of multiples of the standard deviation, the mean being zero Upon such a coordinate system, a normal curve will plot to a straight line We now draw the line which is to represent $\Phi(x)$ through the crossing points of the ordinates at two specified multiples of σ with the horizontals at the corresponding percentages Thus, the crossing points of the ordinates $-\sigma$ and $+\sigma$ have as their corresponding percentages 16 per cent and 84 per cent approximately, according to the probability integral This gives the first term in the normal development of $W(x)$

For the following terms, we must first obtain the coefficients c_r Since for the normal development $c_0 = 0$, $c_1 = 0$, we must get c_2 and, if possible, c_3 as the most characteristic parameters for the divergence from normal In order to calculate these coefficients by the formulae 13, we must transform the moments or averages as they result in polymer work *i e* the moments about zero, into the corresponding ones about the mean This is done as follows

$$\begin{aligned} \mu_1 &= \mu_1' - a_1 = 0 \\ \mu_2 &= \mu_2' - a_1^2 = \mu_2' - (\mu_1')^2 \\ \mu_3 &= \mu_3' - 3\mu_2'a_1 + 2a_1^3 \\ \mu_4 &= \mu_4' - 4\mu_3'a_1 + 6\mu_2'a_1^2 + 3a_1^4 \end{aligned} \qquad (14)$$

Substitution of the quantities μ_3 μ_4 into the formulae 13 gives the coefficients c_r These are now multiplied by $p_r(x)$, the Hermite polynomials of successive order

$$\begin{aligned} p_0(x) &= 1 \\ p_1(x) &= 2x \\ p_2(x) &= 4x^2 - 2 \\ p_3(x) &= 8x^3 - 12x \\ p_4(x) &= 16x^4 - 48x^2 + 12 \end{aligned} \qquad (15)$$

where x is the standardized value of the variable $(X - \bar{X})/1{\cdot}414\sigma$

The sum of these products over all the r's is then multiplied by $(1/\pi^{\frac{1}{2}})\exp(-x^2)$ The result of these operations is the correction term which is to be added algebraically to $\Phi(x)$ for the specified value of x, along the Y axis *i e* along the Gaussian probability integral ordinate of the probability graph Proceeding in this way step by step, for say ten to fifteen equally spaced values of the variable, we obtain the probability graph of the cumulative curve which is then transformed into the ordinary graph for the cumulative curve

Illustration – As experimental data we use again the average molecular weights of polystyrene[12], obtained by ultracentrifuge measurements

$$M_n = 146{,}000 \qquad M_z = 464{,}000$$
$$M_w = 289{,}000 \qquad M_{z+1} = 705{,}000$$

Forming the products $M_zM_w = 1{\cdot}341 \times 10^{11}$, $M_{z+1}M_zM_w = 9{\cdot}45 \times 10^{16}$, gives the second and third moments about zero respectively, which are transformed into the moments about the mean

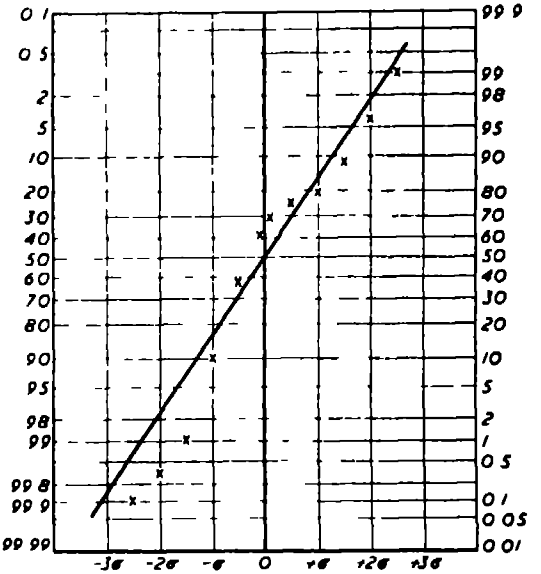

Figure 1 *Estimated distribution curve of molecular weights referred to a Gaussian coordinate system*

μ_2 and μ_3 by using formulae 14. They result as 5.058×10^{10} and 2.657×10^{16} respectively. The square root of the former, 2.249×10^5, is the standard deviation of the weight distribution. Since $c_3 = 1/3!\,(2)^{3/2}\,(-\mu_3/\sigma^3)$, we obtain it by substituting 2.657×10^{16} for μ_3, and 1.138×10^{16} for the cube of σ, as -0.1377. Although it is a disadvantage not to be able to calculate more than this term—since no higher moments are available—yet the series is such that the essential outline of the distribution is represented by the first few terms and often even by the first term. We may, therefore, use the normal development

$$W'(x) = \Phi(x) + (1/\pi^{\frac{1}{2}}) \exp(-x^2)[-0.1377\,p_2(x) + \dots]$$

for calculating the distribution.

Multiplying c_3 by the Hermite polynomial $4x^2 - 2$, and further by the factor $(1/\pi^{\frac{1}{2}}) \exp(-x^2)$, where x is always understood to be in standardized form, we get the correction terms

x (as multiple of σ)	Correction per cent for normal frequencies
± 0.1	+ 1.5
± 0.5	+ 6
± 1.0	− 5.7
± 1.5	− 5.7
± 2.0	− 2.0
± 2.5	− 0.4

These quantities are deviations of the cumulative curve representing the experimental distribution, from the normal cumulative curve (*Figure 1*).

In order to obtain the ogive or cumulative curve in its usual form, to compare it with the experimental curve, we translate the deviations given in multiples of σ into the absolute values of molecular weights. Considering that negative values are excluded, zero being the lowest possible molecular weight theoretically, the part of the distribution on the left of the mean $M_w = 289\,000$ reaches down to about -1.285σ since $\sigma = 224\,000$, which point must be taken as the origin. The cumulative curve is then step by step translated into the cumulative molecular weight curve.

Deviation in terms of multiples of σ	Cum %	Molecular weights
− 2.5	0.1	
− 2.0	0.3	
− 1.5	1.0	
− 1.0	10.0	64,100
− 0.5	37.0	176,550
− 0.1	61.0	266,510
+ 0.1	69.0	311,490
+ 0.5	75.0	401,450
+ 1.0	79.0	513,900
+ 1.5	88.0	626,350
+ 2.0	96.0	738,800
+ 2.5	99.0	851,250

Plotting the cumulative percentages of the second column against the molecular weights of the third column, we obtain the graph, *Figure 2*, which appears a reasonably good approximation to the experimental curve, considering that only the first term in the expansion was used.

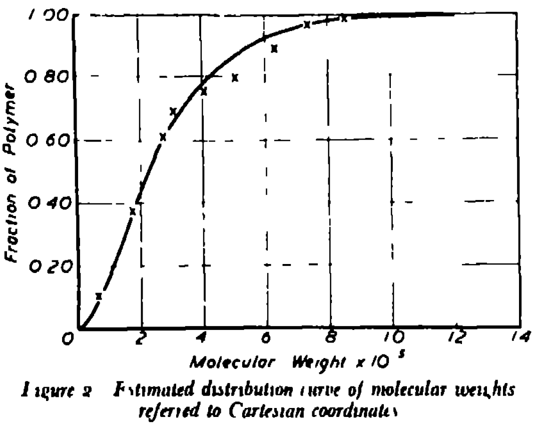

Figure 2 *Estimated distribution curve of molecular weights referred to Cartesian coordinates*

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Thermodynamic Tests for Vapour-Liquid Equilibrium Data on Ternary Systems with Some Comments on Extractive Distillation

E F G HERINGTON, A R C S D I C , Ph D

Methods for testing the internal consistency of isothermal data on the vapour-liquid equilibria in two phase ternary systems are developed by an argument based on thermodynamics and it is shown how these tests can be extended to the study of isobaric data An average value of the logarithm of the relative volatility ratio for two components at a fixed mol fraction of the third is defined and equations for calculating this quantity from binary data are deduced This function is a useful guide to the choice of a third component in extractive distillation

THE difficulty of accurately analysing multicomponent mixtures and the necessity for interpolating experimental data on vapour-liquid equilibria in ternary systems makes some satisfactory test of the consistency of such data very desirable

Tests previously suggested either depend on examining the 'smoothness' of the data, as for example by the method of plotting recommended by COLBURN and SCHOENBORN[1], or require that the data should fit some special type of function, a method exemplified in the use of the van der Waals empirical equation of state by WHITE[2], and in the more general examples of curve fitting discussed by WOHL[3]

In the present paper tests for the consistency of ternary data will be developed by thermodynamic reasoning which assumes only that vapours of the volatile components obey the ideal gas laws and that the molar volume of the liquid mixture is small compared with that of the vapour These tests are similar to that recently discussed for binary systems[4, 5] and resemble it in being strictly applicable only to isothermal data Experimental results are assembled to illustrate that in fact the tests can often be applied usefully to vapour-liquid data determined under isobaric conditions

An increasing interest has recently been shown in extractive distillation which is a technique whereby a third high boiling component is added to a binary mixture in order to modify the volatility ratio of the more volatile pair Several discussions of the mode of choosing the best third component have appeared[1, 6] COLBURN and SCHOENBORN[1] have stated that the relative volatility α, of the two volatile components will vary with the concentration of the third component and also with the ratio of the volatile pair yet DUNN, MILLAR, PIEROTTI, SHIRAS and SOUDERS[7] have suggested that selection of the best third component can be made on the basis of data determined on mixtures containing equal parts of the two volatile components, while UPDIKE, LANGDON and KEYES[8] have discussed the choice of the third component from the results of the study of very few concentrations

In the present paper it is submitted that the average value of $\log \alpha$ for all concentrations of the two volatile components at a fixed molar concentration in the liquid of the third component should be a more useful guide to the selection of a high boiling solvent than a single value of $\log \alpha$ obtained at some arbitrarily chosen concentration Finally, it will be demonstrated that this average value of $\log \alpha$ can be calculated from volatility data on the two binary mixtures containing the third component or, where the third component is not volatile, from activity data on these binaries

DERIVATION OF THE BASIC EQUATION

The symbols employed have the following significance

N_1, N_2 and N_3	are the mol fractions of components 1, 2 and 3 in the liquid phase ,
p_1^0, p_2^0 and p_3^0	are the vapour pressures of pure components 1, 2 and 3 ,

p_1, p_2 and p_3 are the partial pressures of the components in equilibrium with the liquid mixture containing N_1, N_2 and N_3 mol fractions of components 1, 2 and 3

In addition for the three vapour-liquid binary systems containing components 1, 2, 1, 3 and 2, 3

$$\alpha_{12} = (p_1/N_1)(N_2/p_2)\ ,\ \alpha_{13} = (p_1/N_1)(N_3/p_3)\ ,\ etc$$
$$\alpha_{12} \times \alpha_{21} = 1\ etc$$

while

α_{12N_3}, α_{13N_2} and α_{23N_1} are the functions corresponding to α_{12} etc but for the ternary vapour-liquid system containing N_3, N_2 and N_1 mol fractions of liquid components 3, 2 and 1 respectively

$\Delta G^E_{N_1 N_2 N_3}$ is the excess molar free energy of mixing of the solution containing N_1, N_2 and N_3 mol fractions of components 1, 2 and 3, over that of an ideal solution of the same composition and
$\Delta G^E_{N_1 N_2}$, $\Delta G^E_{N_1 N_3}$ and $\Delta G^E_{N_2 N_3}$ are the corresponding excess molar free energies for the binaries containing components 1, 2, 1, 3 and 2, 3

All the above are for a temperature T°abs

Where the vapours obey the ideal gas laws, the total pressure on the system being that of the vapour phase, and where the molar volumes of the liquids are negligible compared with those of their vapours, $\Delta G^E_{N_1 N_2 N_3}$ is given by equation 1 (for a derivation of the free energy of mixing see PARTINGTON[9])

$$\Delta G^E_{N_1 N_2 N_3} = RT\left\{N_1 \ln \frac{p_1}{N_1 p_1^{\circ}} + N_2 \ln \frac{p_2}{N_2 p_2^{\circ}} + N_3 \ln \frac{p_3}{N_3 p_3^{\circ}}\right\} \tag{1}$$

Differentiation of equation 1 with respect to N_1 at constant T and N_3 and combination with condition 2 yields formula 3

$$(N_1 \partial \ln p_1 + N_2 \partial \ln p_2 + N_3 \partial \ln p_3)_T = 0 \tag{2}$$

$$\left\{\frac{\partial \Delta G^E_{N_1 N_2 N_3}}{\partial N_1}\right\}_{T N_3} = RT\left\{\ln \alpha_{12N_3} - \ln \frac{p_1^{\circ}}{p_2^{\circ}}\right\}_{N_3} \tag{3}$$

Equation 2 is the form of the Duhem-Margules equation applicable when the molar volume of the liquid can be neglected with respect to the vapour and is not then restricted to constant total pressure (see CLARK[10] for a recent discussion of equation 2) Integration of equation 3 between the limits N_1', N_2', N_3 and N_1, N_2, N_3 (*i e* along a line of constant N_3) gives equation 4 which is the theoretical basis of the tests

$$\Delta G^E_{N_1 N_2 N_3} - \Delta G^E_{N_1' N_2' N_3} = RT\left\{\int_{N_1'}^{N_1}\left(\ln \alpha_{12N_3} - \ln \frac{p_1^{\circ}}{p_2^{\circ}}\right) dN_1\right\}_{N_3} \tag{4}$$

APPLICATION OF THE BASIC EQUATION TO TESTING EXPERIMENTAL DATA FOR CONSISTENCY

General discussion— If vapour-liquid composition data are available for ternary mixtures covering the whole range of possible compositions of components 1 and 2 at some constant mol fraction of component 3, then equation 5 is the form of equation 4 which is applicable to these conditions because in this case $N_1 = N_2' = 1 - N_3$ and $N_1' = N_2 = 0$

$$\Delta G^E_{N_1 N_3} - \Delta G^E_{N_2 N_3} = RT\left\{\int_0^{1-N_3}\left(\ln \alpha_{12N_3} - \ln \frac{p_1^{\circ}}{p_2^{\circ}}\right) dN_1\right\}_{N_3} \tag{5}$$

Equation 5 can be used to test whether the ternary data at $N_3 = N_3$ (a constant) are consistent with data on the binary systems by the following procedure The functions under the integral sign in equation 5 are plotted using the ternary experimental data, and the area corresponding to the integral is computed The area so found is multiplied by RT If the ternary data are consistent with those for the binaries then the quantity thus obtained should be equal to the difference between $\Delta G^E_{N_1 N_3}$ and $\Delta G^E_{N_2 N_3}$ In the practical computation of these excess free energies for the binary solutions two main types arise, depending on whether the third component is volatile or non-volatile

Derivation of equations applicable to volatile third component— If the total pressure of the binary system is known and the composition of the vapour has been measured for the liquid concentration $N_1 = 1 - N_3$ then the partial pressures of the components over the solution can be computed and $\Delta G^E_{N_1 N_3}$ calculated[8] by the aid of equation 6

$$\Delta G^E_{N_1 N_3} = RT\left\{N_1 \ln \frac{p_{13}}{N_1 p_1^{\circ}} + N_3 \ln \frac{p_{31}}{N_3 p_3^{\circ}}\right\} \tag{6}$$

where p_{13} and p_{31} are the partial pressures of components 1 and 3 over the binary 1 3 at composition $N_1 = N_1$ and where for the present purposes $N_1 = (1 - N_3)$ There is a similar equation for $\Delta G^E_{N_2 N_3}$ involving N_2, p_{23}, p_{32} etc The consistency of data may thus be checked by comparing the difference between these free energies with the value of the integral in equation 5 If, however, the total pressures of the binary mixtures have not been recorded but α_{31} and α_{32} have been measured at a series of liquid compositions then it has been shown previously[4, 8] that the molar excess free energies of mixing of the binaries can be calculated from equations 7a and 7b

$$\Delta G^{E}_{N_1 N_3} = RT\int_0^{N_3}\left(\ln \alpha_{3,1} - \ln\frac{p_3}{p_1}\right)dN_3 \tag{7a}$$

$$\Delta G^{E}_{N_2 N_3} = RT\int_0^{N_3}\left(\ln \alpha_{3,2} - \ln\frac{p_3}{p_2}\right)dN_3 \tag{7b}$$

Substituting equations 7a and 7b in equation 5 gives equation 8

$$\int_0^{N_3}\left(\ln\alpha_{3,1} - \ln\frac{p_3}{p_1}\right)dN_3 - \int_0^{N_3}\left(\ln\alpha_{3,2} - \ln\frac{p_3}{p_2}\right)dN_3 = \left[\int_0^{1-N_3}\left(\ln\alpha_{1,2,N_3} - \ln\frac{p_1}{p_2}\right)dN_1\right]_{N_3} \tag{8}$$

If the isothermal data for the binary systems are consistent then the equalities given by equation 9 are valid[4, 8] and there are corresponding expressions involving $\alpha_{3,2}$ and $\alpha_{1,2}$ so that any suitable alternative expression can be chosen for insertion in the left hand side of equation 8 See next section but one for a discussion of the advantages of using this alternative expression when isobaric data are being studied

$$\int_0^{N_3}\left(\ln\alpha_{3,1} - \ln\frac{p_3}{p_1}\right)dN_3 = -\int_{N_3}^{1}\left(\ln\alpha_{3,1} - \ln\frac{p_3}{p_1}\right)dN_3 \tag{9}$$

If now all the isothermal binary and ternary data are consistent equation 8 must hold Thus the practical application of equation 8 will consist in making plots of experimentally determined values of the various expressions under the integral signs against N_3 or N_1 between the appropriate limits and comparing the relationships among the areas bounded by these curves with the requirements of equation 8 Care must be taken in ascribing the correct algebraic signs to the areas We may note that the sign of any area is the same as that of the function to be integrated provided the upper limit of the definite integral is numerically greater than the lower, while if the upper limit is less than the lower then the converse is true An example of the application of this test to experimental values will be worked out later

Derivation of equation applicable to non-volatile third component— If the third component is not volatile *e g* an inorganic salt, then the basic equation 4 is still true because under these conditions the term $\ln(p_3/N_3p_3^\circ)$ in equation 1 can be replaced by $\ln(f_3/N_3f_3^\circ)$ where f_3, f_3° are the fugacities of component 3 in the mixture and in the pure state respectively Then $\partial \ln f_3$ replaces $\partial \ln p_3$ in equation 2 and equation 4 follows as previously However if component 3 is not volatile, the quantities $\Delta G^E_{N_1 N_3}$ and $\Delta G^E_{N_2 N_3}$ which are required for substitution in equation 5 in order to carry out the test cannot be determined by means of equation 6 nor by equations 7a and 7b, but they can be calculated[11] from equations 10a or 10b Thus

$$\Delta G^{E}_{N_1 N_3} = RT[N_1 \ln\gamma_{N_1, N_3} + N_3 \ln\gamma_{N_3, N_1}] \tag{10a}$$

$$\Delta G^{E}_{N_2 N_3} = RT[N_2 \ln\gamma_{N_2, N_3} + N_3 \ln\gamma_{N_3, N_2}] \tag{10b}$$

where $N_1 = N_2 = (1 - N_3)$ and the standard states for all the activity coefficients are the pure components at the temperature and pressure of the system γ_{N_1, N_3} is the activity coefficient of component 1 in the binary mixture containing N_1 mol fraction of component 1 and N_3 mol fraction of component 3 and similarly for the other coefficients These activity coefficients can be determined for the binary solutions by any of the well established procedures *e g* from measurements of vapour pressure *etc*

A numerical example of the application of equation 8 to an isobaric system containing a volatile third component— Isobaric data are of interest in distillation problems while the tests here developed are strictly applicable only to isothermal conditions but may be applied to isobaric data in a semi-qualitative way[8]

If one of the components *e g* component 3, *Figure 1*, boils at a higher temperature than the other two, then frequently isobaric data across some section AB at constant N_3 will approximate to isothermal data

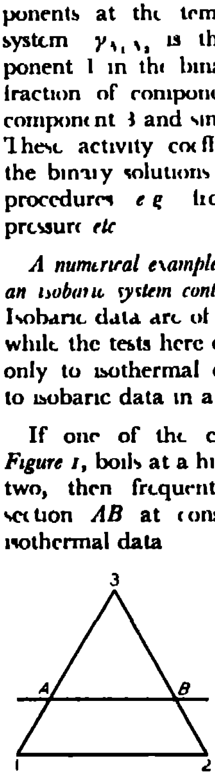

Figure 1 Liquid compositions on a triangular diagram

Sometimes when isobaric conditions are being examined it may be preferable to carry out the calculation of excess free energy for the binary mixtures (equations 7a and 7b) by integrating from pure component 3 to A and component 3 to B (*Figure 1*) using the equality in equation 9 rather than carrying out the integration from 1 to A or 2 to B This method of computation will be preferred when AB is close to 3 for under these conditions the triangle $AB3$ will generally represent more nearly isothermal data under isobaric conditions than the area $AB21$

The experimental work chosen as example is that of BAKER *et alii*[12, 13] on the ethanol-cellosolve-water

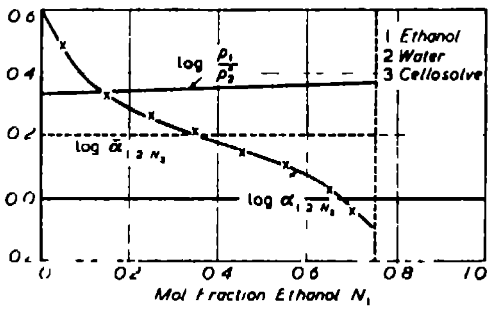

Figure 2a Data for ternary system ethanol-cellosolve water at constant cellosolve N_3 = 0.25 mol From Baker et alii[12, 13]

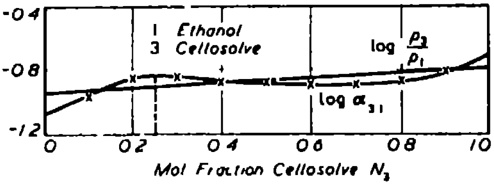

Figure 2b Data for binary system cellosolve-ethanol From Baker et alii[12, 13]

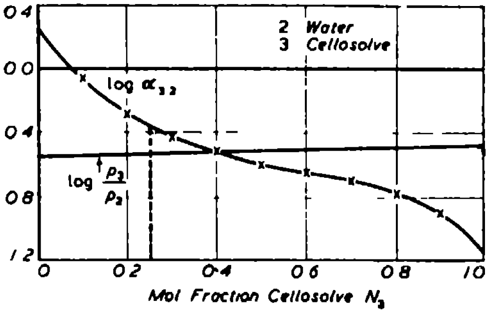

Figure 2c Data for binary system cellosolve-water From Baker et alii[12, 13]

system The boiling points of the components at 760 mm mercury are 78.4°C, 135.1°C and 100°C respectively (Cellosolve is 2-ethoxy ethanol.)

The required values of p_1°, p_2° and p_3° were taken from the following sources The vapour pressure of water was interpolated from published tables[14] The values for ethanol were taken from the collected data of STULL[15] and those of cellosolve from a paper by GARDNER[16]

The test will now be used to determine whether the volatility data for the solutions containing 25 mol per cent cellosolve as plotted in the published paper[13] in the form of two graphs are consistent with the values for the binary solutions The composition values read from the published graphs have been used to calculate log α_{12N_3}, log α_{31} and log α_{32} ($N_3 = 0.25$) and the values so found are plotted against composition in *Figures 2a*, 2b and 2c The components ethanol, water and cellosolve have been labelled 1, 2 and 3 respectively The data are isobaric and not isothermal so that log (p_1°/p_2°) varies with the boiling point The values of log (p_1°/p_2°) shown in *Figure 2a* at the concentrations 0 and 0.75 mol fraction ethanol are the values of this function at the boiling points of water and ethanol respectively The rise in boiling point due to the presence of cellosolve has been neglected here and this treatment was adopted because the boiling points of the binaries are not recorded The values of log (p_1°/p_2°) for these extreme compositions have been joined by a straight line The functions log (p_3°/p_1°) and log (p_3°/p_2°) (*Figures 2b* and 2c) have been calculated similarly

The areas on the graphs were determined by Gauss' method with the results summarized in *Table I*

Table I System ethanol-cellosolve-water— Areas for cellosolve mol fraction = 0.25 *i e* $N_3 = 0.25$

From *Figure 2b*

$$\int_0^{N_3} [\log \alpha_{31} - \log (p_3^\circ/p_1^\circ)] dN_3 = -0.0003$$

From *Figure 2c*

$$\int_0^{N_3} [\log \alpha_{32} - \log (p_3^\circ/p_2^\circ)] dN_3 = +0.1099$$

Hence the left hand side of equation 8 which is equal to the algebraic difference between these quantities = −0.1102

From *Figure 2a*

$$\left[\int_0^{1-N_3} [\log \alpha_{12N_3} - \log (p_1^\circ/p_2^\circ)] dN_1\right]_{N_3} = -0.1089$$

Hence the right hand side of equation 8 = −0.1089

The difference between the two sides of equation 8 = 0.0013

This difference is equivalent to 1.2 per cent of the total area involved

Clearly the ternary data at this composition are consistent with those for the two binaries

EXTRACTIVE DISTILLATION AND THE DEFINITION OF $\ln \alpha_{12N_3}$

We shall confine our attention to liquids which are completely miscible at their boiling points The behaviour of a three component system under isothermal distillation or rectification is only completely defined when a pair of the volatility ratios is known in terms of all the liquid concentration variables However, for some purposes *e g* in extractive distillation, an average value of α for the volatile pair at a constant concentration of the third component has been used and this quantity has in the past been estimated from the mean of a few experimentally determined values of vapour composition of the ternary system[17]

We shall consider here an average value of ln α instead of an average value of α because the logarithmic function is more fundamental to distillation theory Such an average will be designated by $\ln \bar{\alpha}_{1\,2\,N_3}$ which is to be interpreted as the average value of $\ln \alpha_{1\,2\,N_3}$ over the whole range of concentration from $N_1 = 0$ to $N_1 = (1 - N_3)$ in the ternary system at a constant concentration N_3 of the third component

This function is defined by equation 11 which follows the normal definition of an average of a continuous function

$$\ln \bar{\alpha}_{1\,2\,N_3} = \left[\left\{\int_0^{1-N_3} \ln \alpha_{1\,2\,N_3}\, dN_1\right\} \Big/ \left\{\int_0^{1-N_3} dN_1\right\}\right]_{N_3} \tag{11}$$

Equation 11 is identical with equation 12 which is the form we will adopt here because of its practical utility

$$\ln \bar{\alpha}_{1\,2\,N_3} = \ln \frac{p_1}{p_2} + \frac{1}{1-N_3}\left[\int_0^{1-N_3}\left(\ln \alpha_{1\,2\,N_3} - \ln \frac{p_1}{p_2}\right) dN_1\right]_{N_3} \tag{12}$$

The integral in equation 12 is identical with that in equation 5 so we may write

$$\ln \bar{\alpha}_{1\,2\,N_3} = \ln \frac{p_1}{p_2} + \frac{1}{1-N_3}\,\frac{1}{RT}\left[\Delta G^E_{N_1\,N_3} \qquad \Delta G^E_{N_2\,N_3}\right] \tag{13}$$

from which it can be seen that $\ln \bar{\alpha}_{1\,2\,N_3}$ can be calculated solely from data on the two binaries

Derivation of equations which may be used to calculate $\ln \bar{\alpha}_{1\,2\,N_3}$ *from binary data when the third component is volatile* – When the total pressure of the binary system is known and the compositions of the vapour have been determined at the liquid compositions in which we are interested, the two equations equivalent to equation 6 can be inserted in equation 13 which after rearrangement gives equation 14

$$\ln \bar{\alpha}_{1\,2\,N_3} = \ln \frac{p_{1\,3}}{p_{2\,3}} + \frac{N_3}{1-N_3} \ln \frac{p_{3\,1}}{p_{3\,2}} \tag{14}$$

where $p_{1\,3}$, $p_{2\,3}$, $p_{3\,1}$ and $p_{3\,2}$ are defined as for equation 6

Alternatively if $\ln \alpha_{3\,1}$ and $\ln \alpha_{3\,2}$ are known as functions of N_3 then equations 7a and 7b can be inserted in equation 13 to give equation 15

$$\ln \bar{\alpha}_{1\,2\,N_3} = \ln\left(\frac{p_1}{p_2}\right) + \frac{1}{1-N_3}\left[\int_0^{N_3}\left\{\ln \alpha_{3\,1} - \ln\left(\frac{p_3}{p_1}\right)\right\}dN_3 - \int_0^{N_3}\left\{\ln \alpha_{3\,2} - \ln\left(\frac{p_3}{p_2}\right)\right\}dN_3\right] \tag{15}$$

Derivation of equation for calculation of $\ln \bar{\alpha}_{1\,2\,N_3}$ *from binary data when the third component is non-volatile* – Equations 10a and 10b can be inserted in equation 13 and after rearrangement this gives equation 16

$$\ln \bar{\alpha}_{1\,2\,N_3} = \ln\left(\frac{p_1}{p_2}\right) + \ln\left(\frac{\gamma_{N_1'\,N_1}}{\gamma_{N_2\,N_1}}\right) + \frac{N_3}{1-N_3} \ln\left(\frac{\gamma_{N_1\,N_1}}{\gamma_{N_1\,N_2}}\right) \tag{16}$$

where $N_1 = N_2 = (1 - N_3)$ and the activity coefficients are as defined for equations 10

Equations 14, 15 and 16 permit the calculation of $\ln \bar{\alpha}_{1\,2\,N_3}$ from binary data, but before illustrating the use of equation 15 by a numerical example we will examine the general properties of $\ln \bar{\alpha}_{1\,2\,N_3}$

General properties of $\ln \bar{\alpha}_{1\,2\,N_3}$ – The following properties of $\ln \bar{\alpha}_{1\,2\,N_3}$ can be directly derived from equations 13 to 16

1 $\ln \bar{\alpha}_{1\,2\,N_3}$ will only be equal to $\ln (p_1^\circ/p_2^\circ)$ if $\Delta G^E_{N_1\,N_3} - \Delta G^E_{N_2\,N_3}$ is zero If one of these free energies is not zero it is unlikely that the other will be equal to it, so we may conclude that in general $\ln \bar{\alpha}_{1\,2\,N_3}$ will only be equal to $\ln (p_1/p_2)$ if both of the binary systems 1 3 and 2 3 are ideal

2 If $N_3' = 0$ then

$$\ln \bar{\alpha}_{1\,2} = \ln (p_1/p_2) \tag{17}$$

Thus the average value of ln α for a binary system is equal to the 'ideal' value of ln α

3 If the mol fraction of a volatile third component be increased then, as this fraction tends to unity $\ln \bar{\alpha}_{1\,2\,N_3}$ tends to a limit for it follows from equation 15 by the usual procedure for finding the limit of a quotient that

$$\underset{N_3\to1}{\ln \bar{\alpha}_{1\,2\,N_3}} = \underset{N_3\to1}{\ln \alpha_{3\,2}} - \underset{N_3\to1}{\ln \alpha_{3\,1}} \tag{18}$$

4 $\ln \bar{\alpha}_{1\,2\,N_3}$ may exhibit a maximum or a minimum as N_3 is increased from 0 to 1

Calculation of $\log \bar{\alpha}_{1\,2\,N_3}$ *from binary data by equation 15*—The system ethanol-cellosolve-water[13] has again been chosen as an example, although it is in fact of no interest in extractive distillation The points marked with a cross in *Figure 3* were calculated from the binary values according to the following procedure The value at 0 0 mol fraction of the third component was derived from equation 17

The value of $\log \bar{\alpha}_{1\,2\,N_3}$ recorded in *Figure 3* for $N_3 \to 1$ was obtained by inserting the limiting values of $\log \alpha_{3\,2}$ and $\log \alpha_{3\,1}$ ($N_3 \to 1$) in equation 18, these values being obtained from *Figures 2b* and *2c* The values plotted for $N_3 = 0.25$, 0.47, 0.68 and 0.88 were derived from the binary data shown in *Figures 2b* and *2c* by using equation 15 The areas up to $N_3 = 0.4$ (*Figure 2c*) were calculated in the positive direction from zero to N_3 mol fraction of component 3 and those above $N_3 = 0.4$ were calculated in the negative direction from 1 to N_3 using the equality in equation 9 This method was adopted in order to minimize the temperature range over which the isobaric data were integrated *Figure 3* indicates clearly that the addition of sufficient cellosolve to an alcohol-water mixture decreases the volatility of alcohol compared with water to such an extent that the alcohol is less volatile than water

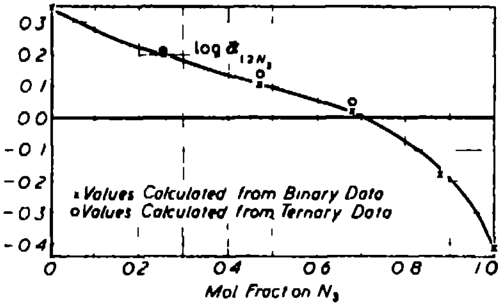

Figure 3 Calculated values of $\log \bar{\alpha}_{1\,2\,N_3}$ *from the binary data compared with the observed All experimental values from Baker et al*[12, 13]

The circles in *Figure 3* are the values of $\log \bar{\alpha}_{1\,2\,N_3}$ calculated from the observed ternary data[14] The value at $N_3 = 0.25$ agrees excellently with the binary values because the ternary data are consistent with those for the two binaries (*Figure 2*) but the agreement for $N_3 = 0.47$ and 0.68 is not so good, part of this discrepancy may arise from the fact that the data are isobaric and not isothermal In *Figure 2a* the value of $\log \bar{\alpha}_{1\,2\,N_3}$ is indicated and may be compared with the value of $\log \bar{\alpha}_{1\,2}$ which is equal to $\log (p_1/p_2)$ (equation 17)

Some remarks on the use of $\ln \bar{\alpha}_{1\,2\,N_3}$—The study of $\ln \alpha_{1\,2\,N_3}$ cannot replace entirely the full investigation of the vapour liquid equilibria in the selection of a suitable solvent for extractive distillation, but a knowledge of $\ln \bar{\alpha}_{1\,2\,N_3}$ certainly gives more information on the behaviour of an extractive solvent than do a few values of $\ln \alpha_{1\,2\,N_3}$ determined at arbitrarily chosen concentrations Since $\ln \bar{\alpha}_{1\,2\,N_3}$ can be computed as a function of N_3 solely from binary data it follows that $\ln \bar{\alpha}_{1\,2\,N_3}$ is a suitable parameter for the preliminary evaluation of an extractive solvent The object of introducing the third component in extractive distillation is to modify the volatility ratio of components 1 and 2 which are difficult to separate in their binary mixture, whence it follows that the most satisfactory third component will in general be one which yields the largest numerical value of the function

$$\log \bar{\alpha}_{1\,2\,N_3} - \log \bar{\alpha}_{1\,2}$$

where component 1 is the component with the highest vapour pressure *i e* $p_1 > p_2$

If the values of this function are small for a given third component then further investigation of this solvent is probably not justified, but if the value is large further experimental exploration of the ternary mixture may be carried out profitably in order to establish how $\log \alpha_{1\,2\,N_3}$ (N_3 constant) varies with the concentration of component 1

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Research Correspondence

A Cleavage Step on Mica with a Height that is a Half-integral Multiple of the Crystal Lattice Spacing

Figure 1 shows the structure of muscovite mica[1-5]. At *q* there is a plane of silicon-oxygen tetrahedra hexagonally linked with the vertices of the tetrahedra pointing up. (Some of the tetrahedra are occupied by aluminium atoms.) At *s* there is a similar silicon-oxygen sheet with the vertices of the tetrahedra pointing down. These sheets are strongly cross-linked at *r* by aluminium atoms and hydroxyl groups are incorporated. The whole crystal is made up of a succession of such double sheets loosely bonded together as at *t*, with potassium atoms in 12-coordination between them. The atoms immediately on either side of the planes passing through the potassium atoms are in mirror image relation. The unit cell reaches from the potassium layer at *p* to the potassium layer at *x*. It has, however, been suggested that the crystal may cleave easily along any of the potassium planes as at *p*, *t* or *x*. The length of the *c* axis, planes *p* to *x* from x-ray data is 20.04 Å, and the perpendicular distance between the planes, $c \sin \beta$, is 19.96 Å. It is to be expected therefore that the height of cleavage steps will be integral multiples of this value or possibly of half this value *i.e.* integral multiples of 19.96 Å or possibly of 9.98 Å.

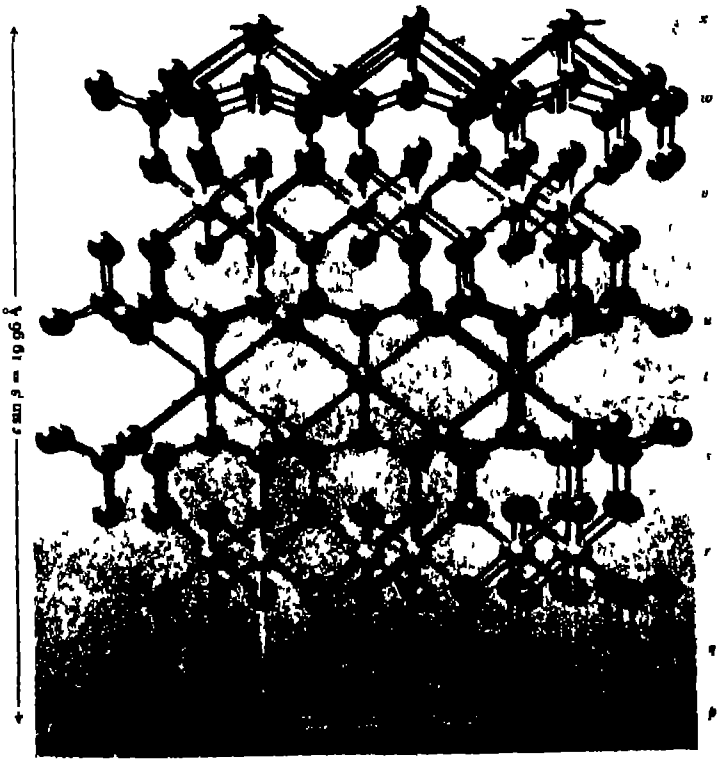

Figure 1. The structure of muscovite mica. View of a model looking approximately along the a-axis. The white threads outline the unit cell. A crystal could cleave easily along the planes of potassium atoms such as at p, t and x.

Work on oriented overgrowths indicated that half-integral cleavage steps might sometimes occur[8-10]. When some crystals are grown on a clean cleaved surface of muscovite mica they all orient with their axes pointing the same way. Occasionally over some part of the mica surface the crystals will all orient with their axes pointing in precisely the opposite direction. This could easily be explained if the atomic structure of the mica surface for this region were the mirror image of that for the remainder of the specimen as would occur if their respective cleavage planes were separated by a half-integral number of lattice spacings.

TOLANSKY, using multiple beam interferometric techniques has measured the heights of a great many cleavage steps but has found in all his measurements that the heights of the steps are integral multiples of twice the minimum distance[9,10]. That is integral multiples of 20 Å. To obtain his results Tolansky measured the displacement of sharpened Fizeau fringes where they crossed the cleavage step. He has estimated that the error for such measurements under favourable conditions is of the order of ± 3 Å, and from the consistency of his figures this would appear to be a conservative claim.

Figure 2 shows the fringes of equal chromatic order[10,11] for a specimen of muscovite mica, silvered on both sides. The line section crosses three facets *P*, *Q* and *R*. For facets *Q* and *R* the order of interference is the same, all the experimental variants are near their optimum for maximum resolution, and the reflection coefficients at the mica/silver interfaces are near 96 per cent so that the width of the interference lines at half maximum intensity is only 1/75 of the spacing of orders. The error of measurement under these conditions is therefore no more

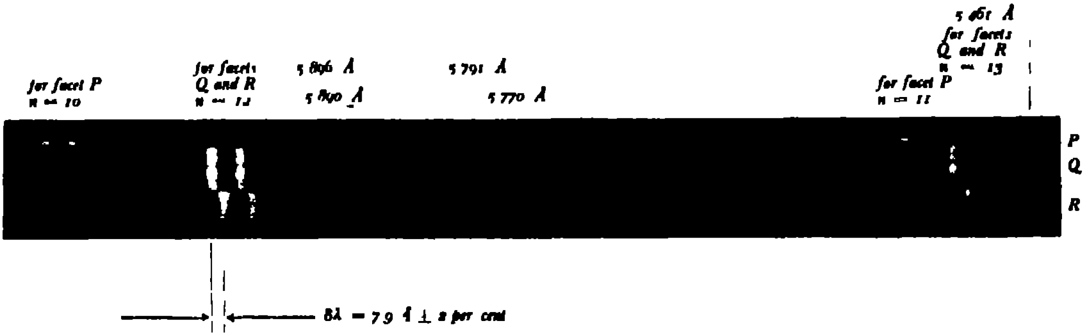

Figure 2 Fringes of equal chromatic order for a line section across three facets P, Q and R of a specimen of muscovite mica At any point of this line section the wavelengths most strongly transmitted are those which satisfy the equation $2\mu t = n\lambda$ The fringes are all doublets because mica is birefringent Where n the order of interference is 12 the displacement of the fringes facet Q to facet R is 2.00 mm ± 0.04 mm The dispersion near the D lines is 3.95 Å/mm The measured height of the cleavage step is therefore $n\delta\lambda/2\mu = 30$ Å ± 1 Å The magnification of lateral dimensions along the line section across the facets is 2 For any given value of n, displacements in wavelength are linearly related to changes in optical thickness of the specimen so that in this photograph the magnification in height and depth is 670,000 Reproduced four fifths of original size

than ± 1 Å The measured value of the displacement of the fringes is 7.9 Å ± 2 per cent The height of the cleavage step is then

$$n\delta\lambda/2\mu = 30\,\text{Å} \pm 1\,\text{Å}$$

Within the value of the experimental error this is just 1.5 times the crystal lattice spacing The result provides direct and unambiguous evidence of the existence of cleavage steps that are half-integral multiples of the crystal lattice spacing and thus resolves the difficulties that otherwise exist in interpretation of the phenomena of oriented overgrowths

I wish to express my thanks to Dr W H Taylor of the Cavendish Laboratory for his advice and for permission to photograph the model of the structure of mica I wish also to thank Dr F P Bowden, F R S, and Professor S Tolansky for their advice and encouragement, Imperial Chemical Industries for provision of the spectograph the Ministry of Supply (Air) for support and the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship

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X-Ray Determination of Mirror Planes and Rotation Axes

CENTRING of unit cells is revealed by systematic absences among the general x-ray reflections, glide planes and screw axes are revealed by systematic absences in a zone or row of reflections, unless masked by general (centring) absences It has recently been found possible, in suitable cases to detect centres of symmetry by a statistical study of the x-ray intensity distribution[1,2], thus increasing considerably the number of space groups identifiable from x-ray evidence alone[3] The statistical study makes it possible to detect also those symmetry elements $(2, 3, 4, 4, 6, 2_1, 4_{1-3}, 6_{1-5})$ that give a centrosymmetric plane projection By the same method it would be possible in theory[3] to detect also those elements $(\bar{2} \equiv m, 3, \bar{4}, \bar{6})$ that give a centrosymmetric line projection, though the small number of reflections corresponding to a line projection does not afford a very satisfactory statistical basis for discrimination

The detection of centrosymmetry depends on rather small numerical differences between the centric and acentric[4] distribution functions Symmetry elements that make two or more equivalent atoms coincide in a plane or line projection, however, produce a gross effect on the *average* intensity of the corresponding zone or row of reflections The average intensity of the general reflections is always given by

$$\langle I \rangle = \sum_{j=1}^{N} f_j^2 \equiv \Sigma$$

where f_j is the scattering factor of the jth atom and the summation is over all atoms of the cell, but the average intensity of reflections corresponding to a projection in which equivalent atoms coincide in groups of n is

$$<I> = \sum_{j=1}^{N/n} (nf_j)^2 = n\Sigma$$

(The effect of coincidence was pointed out some time ago[4], but its importance was not realized) A mirror plane ($\bar{2}$), therefore, will have a zone of reflections with average intensity twice as great as that of the general average , rotation and certain screw axes will have rows with average intensity up to six times as great This is a much greater numerical effect than that involved in the detection of centres of symmetry and should be particularly useful for the determination of mirror planes

My thanks are due to Dr D Rogers, whose unpublished work on the effect of symmetry elements on Patterson syntheses suggested this note

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Gene Mutations Induced by Camphor in Yeast

SPONTANEOUS occurrence of tetraploidy has been repeatedly observed in our two chromosomic brewery yeast[1-4] and it has been found easy to duplicate the chromosome complement by physical and chemical agencies under appropriate conditions[4-9] On theoretical grounds it appeared questionable whether the so-called C-mitosis had anything to do with the actual induction of tetraploidy Many substances have been known to induce C-mitosis[9,10] but only a few are capable of producing stable tetraploids Inhibition of the anaphase separation does not necessarily mean that the cell should become a tetraploid It is stated[11] that the doubling of the chromosome complement produces a change in the norm of reaction of the organism, and its effect is in this respect analogous to that of a gene mutation ? Is polyploidy the result of a gene mutation enabling the duplicated chromosome complement to function harmoniously ? If that is so, it stands to reason that only those substances among the groups inhibiting the normal course of cell division, which are capable of producing the specific gene mutation, can give stable tetraploids Cold shock which induces polyploidy in yeast[6,12] also induces gene mutations[3] Any assumption that the harmonious working of the duplicated chromosome complement should be preceded by a specific gene mutation necessitates as a corollary that polyploidogens should be capable of producing other gene mutations as well[14] Experimental evidence supporting such a probability was obtained during a series of investigations on the effect of camphor on yeast

Treatment of actively dividing cells with camphor for 45 days about two years ago enabled isolation of stable autotetraploids[8] During an analysis of the various causes which may have contributed to the failure of the earlier investigators to isolate stable tetraploids[14-16] evidence was obtained that camphor produces also gene mutations

Figure 1 shows a giant colony of the control at the start of the experiment It could be classified as *Rough II* (*cf* *Photo 10*) The colony shows two small *Smooth II* sectors at its periphery indicating that these are the results of mutations during the later stages of growth of the colony Immediately after giant colony inoculation, a loop from the culture was inoculated into sterile wort containing a drop of a concentrated solution of camphor in absolute alcohol The quantity of camphor to be added was determined experimentally, based on the criterion that at the end of growth for 24 hours a good crop should be obtained The giant colony grown from material cultured in the presence of camphor for 24 hours is presented as *Figure 2* The colony shows *Smooth I*, *Smooth II* and *Rough II* sectors indicating that camphor has induced gene mutations These mutations have already been shown to occur spontaneously[8] and it appears that as with exposure to ultraviolet irradiation[17,18] camphor has merely increased their rate of incidence

When camphor which induces autotetraploidy produces gene mutations as well, it appears that a gene mutation at a specific locus should precede a doubling of the chromosome complement Acceptance of the above suggestion would offer a rational explanation as to why not all substances inhibiting normal cell division are capable of inducing polyploidy They are probably incapable of producing the specific gene mutation The reverse may apply in animals where polyploidy is generally absent and where even known polyploidogens do not induce a chromosome doubling Colchicine has been suspected to produce gene mutations in *Daphnia*[19] and hence the fact that treatment with colchicine does not induce polyploidy in animals may be the result of the absence of the specific locus, mutations in which alone can enable the duplicated chromosome complement to function harmoniously

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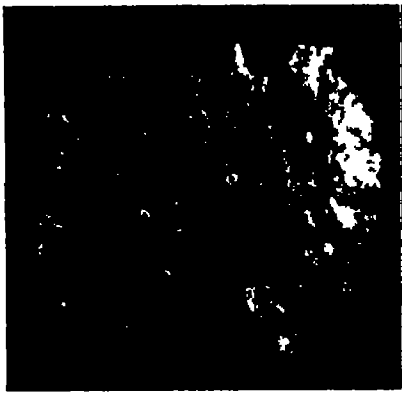

Figure 1 BT 1 (12/10/45) grown on barley malt agar 16 day growth 3 5 cm Photographed on 8/9/49

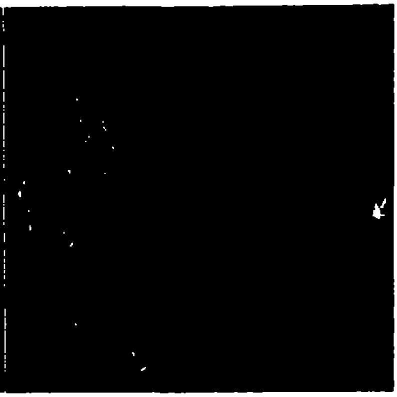

Figure 2 After an initial growth of 24 hours in wort containing camphor Barley malt agar 15 day growth 4 2 cm Photographed on 8/9/49

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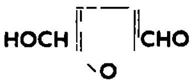
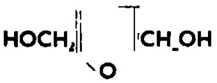
2,5-Bishydroxymethylfuran

IT was demonstrated by MIDDENDORP[1] that 5-hydroxymethylfurfural *I* undergoes the Cannizzaro reaction and gives rise to 5-hydroxymethylfuran 2-carboxylic acid and 2 5-bishydroxymethylfuran *II* In our experience, however while the former compound is obtained readily enough by this procedure, the preparation of the 2,5-bishydroxymethylfuran is difficult Since the hydrogenation of 5-hydroxymethylfurfural proceeds smoothly giving good yields of 2,5-bishydroxymethyltetrahydrofuran *III* we considered that it might be possible to find conditions whereby only the aldehyde group of 5-hydroxymethylfurfural was reduced and in this way to prepare the bishydroxymethylfuran *II*



(*I*)



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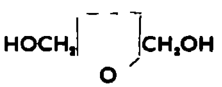

(*III*)

The conversion of 5-hydroxymethylfurfural *I* into 2,5-bishydroxymethyltetrahydrofuran *III* was accomplished by HAWORTH, JONES and WIGGINS by heating *I* in ethereal solution with hydrogen and Raney nickel at 130°C and 75 atm pressure for 6 hrs It has now been found that if the hydrogenation is carried out under less drastic conditions, particularly at 75°C and 100 atm pressure, then a mixture of products is obtained which consists of 2,5-bishydroxymethylfuran and unchanged 5-hydroxymethylfurfural from which the former compound crystallizes

The table given opposite indicates the proportions of the products *I*, *II* and *III* obtained under different conditions of hydrogenation

The 2,5-bishydroxymethylfuran obtained by the hydrogenation of 5-hydroxymethylfurfural formed needles when recrystallized from chloroform It had m pt 75 5-77°C (Found C, 56 4, H, 6 0 Calc for $C_6H_8O_3$ C, 56 2, H, 6 2 per cent) Middendorp recorded m pt 80°C for this substance On

Wt of 5 hydroxy-methyl furfural	*Temp*	*Press*	*Time*	*Wt of products gm*		
				Recovered 5 hydroxy methyl furfural	*2 5 bis hydroxy methyl furan*	*2 5 bis hydroxy methyltetra hydrofuran*
gm	*°C*	*atm*	*hr*			
38	25	72	8	28	–	—
28	75	100	4	18	9.5	–
31	160	78	4	—	2	27

The yield of recovered 5 hydroxymethylfurfural is sometimes low because this material often decomposes excessively during distillation

being treated with benzoyl chloride in pyridine solution it formed a characteristic dibenzoyl derivative which, after recrystallization from alcohol, had m pt 76–77°C (Found C, 71.8, H, 4.8 $C_{20}H_{16}O_5$ requires C, 71.5, H, 4.8 per cent)

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Emission of Infra-red Radiation by Metallic Powders

THE possibility of using 'ionic' crystals or powders as sources of infra-red radiation in the range of wavelengths which they absorb strongly has been considered by FROHLICH[1] who has shown that an electron passing close to a particle excites a dipolar oscillation yielding radiation of wavelengths comparable with the particle size For efficient radiation it is necessary to have a high density of electrons as present in a spark or arc discharge, and to suspend the particles in the discharge plasma The particle concentration must also be large

Experiments have been made using inorganic and metallic powders of various particle sizes to obtain preliminary information on the distribution of the radiation wavelengths, the effect of particle size on the radiation and the possibility of using this technique as a source of long wavelength radiation The present note describes briefly the experimental technique and results for the metallic powders

A high electron density was obtained by using a repetitive 6 kv spark at 80 amp, 200 times per second, the duration of each spark was approximately 5 × 10^{-6} second The powder was allowed to flow freely into the discharge either down the centre of an electrode or through a separate feed perpendicular to the direction of the spark The formation of clusters of particles becomes more probable as the particle size is decreased but is reduced by initial drying and the violence of the discharge

The radiation was focused by means of a spherical front-silvered mirror on to the element of a semi-conductor type of bolometer used in one arm of a bridge network The bridge and all connecting leads were shielded from stray electrical interference due to the spark The bridge was adjusted for optimum bolometer sensitivity corresponding to an element current of 10^{-5} amp and the power sensitivity measured under these conditions was found to be 100 ± 5 μw/1 per cent change of resistance A glass plate (G P) 1 mm thick was used between the source and the bolometer as a filter to reject wavelengths greater than 5μ and a high melting point paraffin wax filter (P W F) to reject wavelengths less than 25μ

Table I shows a selection of the results obtained for several sources, the filament results being obtained for comparison with spark and metallic powder results The figures shown are corrected for the fact that only a fraction of the radiation is picked up by the mirror and the fact that the image focused on the bolometer element is greater than the area of the element Each figure is the mean value for 10 experiments and the scatter about the mean is of the order of ± 20 per cent for the spark or powder radiation and ± 5 per cent for the filament radiation

Table I

Source	*Total radiation (No filter)*	*Total radiation transmitted*	
		by G P	*by P W F*
Spark	18 mw	44	38
Copper powder (0–60μ)	65 mw	-	13
Copper powder (90μ)	7 mw		
Copper powder 180μ)	*None detected*		
Hot filament	240 mw	31	18

The results exhibit the following features

1 the powers are all comparable in order of magnitude but whereas the filament is a steady source the spark is an intermittent one, and the corresponding 'peak' powers radiated may be larger by a factor of 10^3 than the mean values detected

2 the radiation efficiency (ratio of power output power input) for the copper powder (50 60μ) is 0.15 per cent compared with 0.45 per cent for the filament

3 an increase in particle size results in a decrease in radiation as predicted by Frohlich

4 the spark shows a similar spectral distribution to that of the filament but the radiation from the powder reveals a marked change in this distribution

An analysis of the distribution of radiation emitted by a black body at 800°C (approx filament temperature) shows approximate agreement with the spark and filament figures except for the percentage of radiation $> 25\mu$ where the measured values are an order of magnitude greater , this is partly due to the paraffin filter having ‘windows’ between 5μ and 7μ and between 9μ and 13μ each permitting 3 per cent transmission, and being translucent for wavelengths $< 5\mu$

The results offer no conclusive evidence for a radiation mechanism which is different to that of a black body but are in agreement with Fröhlich's theoretical predictions The possibility of utilizing the apparently high peak powers is attractive

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Dipole Moment of 1,2,3,4,5,6-Hexachlorocyclohexane

ATTEMPTS have been made to draw conclusions concerning the structure of the stereoisomeric benzene hexachlorides from dipole moments measured in solution[1] but without much success Today the structures of those substances have all been determined by interferometric methods [2, 3] (electron diffraction–x-ray analysis) and it has been pointed out that the sequence of dipole moments corresponds to that to be expected from the known structures[2] Even if the moments had been measured in the vapours, however, it would not be possible today to check quantitatively the structures by computing theoretical dipole moments

New determinations of the dipole moments of the α, β, γ and δ isomers have been published recently by KULKARNI JATKAR and KULKARNI[4] who made the measurements in solution and computed the moments using a simplified formula The results do not, however, agree with values earlier reported In *Table I* some reported values of dipole moments measured in benzene solution are listed, together with the new values MELANDER's value for the δ isomer refers to a single measurement only

Table I Dipole Moments in D Units

	Earlier values[1 5 8]			*Recent values*[4]
α	2 20 (1930)[5]	2 15 (1931)[6]	2 22 (1947)[8]	1 73
β	0 (1930)[5]	0 (1932)[7]	0 (1947)[8]	0 00
γ	3 6 (1946)[1]		2 89 (1947)[8]	2 53
δ	0 (1946)[1]		2 17 (1947)[8]	0 00

The most serious discrepancy occurs for the δ isomer for which zero moment is reported The structure of this compound (*εεεεεκ*) seems indeed to exclude this possibility

We have repeated the measurements on this compound using a new apparatus, and could only confirm HETLAND's results It seemed possible that the substances measured in our laboratory and in Bangalore were not identical, and we wished to control the identity of our substance which was kindly offered us a few years ago by Imperial Chemical Industries Ltd , it has a m pt 138° C We are therefore much indebted to BIJVOET in Utrecht who is working out the crystal structure of the δ isomer for his kindness in placing a small sample of his substance at our disposal Melting points of the two substances and of mixtures of both clearly prove that Bijvoet's and our substances are indeed identical As a further check, however, an x-ray rotation diagram about the monoclinic *b* axis of a crystal prepared from our sample was taken and a lattice constant determined which is identical with that found by Bijvoet It therefore seems quite obvious that Hetland's measurements have been carried out on the pure δ isomer

We feel it necessary to publish this note because the discrepancy mentioned might otherwise cause distrust in Hetland's measurements or even in the correctness of the interferometrically determined structure of the δ isomer

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Commentary: *Higher Education for Technologists*

THE TEMPO of wartime developments has stimulated a variety of discussions and plans for the future teaching of scientific technologists. Current conditions may well delay any implementation of plans to provide for British needs in this field of higher studies. They may even lead to the adoption of patchwork schemes which appear to be economical, but which fail to provide any real impetus in applying scientific knowledge to our economic necessities. Bolder provision for advanced technological studies could have such important consequences that the current discussions and controversies deserve careful examination.

Two fundamental ideas can be distinguished in such discussions. In principle these two guiding ideas are concerned with very different values, though in practice their consequences are closely intertwined.

On the one hand, the view is held that higher studies in scientific technology are educationally narrowing, and form a far less satisfactory foundation for responsible citizenship than, say, higher studies in one of the humanities. On the other hand, the view is put forward that British industry needs more numerous and more highly trained technologists if the material standard of life in Britain is to be improved, or even maintained. Both these views are concerned with the practical problem of how far a segregation of technological from academic studies is desirable.

In Britain the current teaching activities of what are variously called colleges of technology, technical colleges, or technical institutes are extremely diversified. Often such activities are the outcome of a long period of growth and adaptation. The empirical experience which is woven into such organizations cannot be lightly disregarded. But the historical fact that the industrial revolution started early in Britain has influenced the structure of technical teaching in ways which are not always best adapted to current conditions, just as it has generated industrial practices which should be obsolete in the present age. The need for highly educated and trained technologists has grown very fast in recent years. It is reasonable to examine how far existing British institutions evolved for teaching technologies at various levels can hope to satisfy this need at the highest level.

The discussion which follows is particularly concerned with technological studies at the highest level, because of their interconnection with university studies. Though the proper organization of technical training at lower levels is quite as important for the public welfare, such organization is governed by quite different considerations which will not be dealt with here.

In discussing the interconnection between higher technological studies and the universities, possible principles of segregation are best examined first, before taking into account some practical considerations.

Starting with the sharpest distinction, it can be argued as a basic principle of segregation that there are two types of higher study which should be infused with a very different spirit To preserve maximum vitality, academic studies must pursue learning for its own sake But advanced technological studies can only be justified when they inspire a continued zeal for the application of basic scientific knowledge to the material substructure of our civilization An academic attitude towards new knowledge does not necessarily shut out an eagerness for practical applications But it is almost a matter of instinct for the scientist, as it is for his fellows working in other fields, that the highest rewards in new knowledge are received for truly disinterested pursuivants The word 'academic' which is often equated with 'unpractical' is honourable in this context only By contrast, to be academic in the practical applications which must inspire technological teaching would argue gross irresponsibility

Because of this necessary difference in spirit, it is quite as important to distinguish between the academic and the technological approach to the sciences, as to distinguish between the sciences and the humanities This description of a fundamental difference between the academic pursuit of knowledge and the practical zeal for its application seems more penetrating and more practically significant for the purpose of the present discussion than the frequently made distinction between humanistic and scientific studies

An exaggerated contrast between the sciences and the humanities as means of higher education may warp the academic attitude towards the technologies It can even be argued that any distinction between the sciences and the humanities, considered as branches of human knowledge forming part of the proper scope of academic studies, is in part a historical accident In the history of university teaching in Western Europe, the humanities to some extent supplanted earlier university disciplines which had a greater emphasis, for example, on divinity In its turn, the study of the humanities has to some extent been supplanted by the study of the natural sciences Brotherly quarrels between the older and the younger are no new thing in the history of learning, and must not be allowed to distort judgements and practical decisions about advanced technological teaching

Before leaving any further considerations about the new-old intellectual battle-game between the sciences and the humanities, it is pertinent to examine the objection that the sciences, even if studied academically as branches of knowledge, have smaller educational value than any of the humanities The isolation and specialized atmosphere of the laboratories is said to separate science students from the experience of humanity If this separation were in fact complete the primary purpose of university education would have failed One of the arguments for centring any specialized study full in the midst of other university activities is to counterbalance the deliberate isolation which specialization requires With the separation of the different branches of knowledge, the risk of narrowness of outlook resulting from too exclusive a pursuit of any one branch is quite general Studies in the humanistic subjects, when these shut out any awareness of scientific disciplines, can hardly be regarded as fitting a student for public responsibilities in contemporary society, any more than scientific studies with no awareness of other branches of knowledge fit the science student for his responsibilities in regard to the great material power which he may administer in later life But even when academic studies are properly balanced, technological studies call for special treatment because of the difference of approach

PRACTICAL ARGUMENTS

Quite apart from the distinction of principle, which would seem to favour segregation of the academic approach to higher studies from the technological approach, there are strong practical arguments in favour of segregation For example, the administration of university affairs and university budgets should be quite distinct from the administration of at any rate the more advanced teaching in the technologies With such very different objectives, men best fitted to serve on the governing body of an institute of advanced technology should have very different qualifications from those most suited to an academic governing body Certain advantages can be recognized in having a limited common membership on the two types of governing body, but the main objectives should be kept quite distinct

EDUCATIONAL AND SOCIAL OBJECTIONS

Although arguments of principle and of effective administration favour the separation of technological from academic studies, in practice there are very strong educational and social objections to a complete segregation These arise mainly from the social and economic background to higher studies, and may not be as strong in other countries In Britain, the growth of higher education has in fact interwoven the academic and the technological spirit of study in important academic disciplines where the vocational element is strong The variety of such vocational courses of study is so large in contemporary university life that it has quite transformed the nineteenth century idea of a university

There may be some risk of distorting the discussion whenever specific examples are examined One example where experience in handling the problem is richest, however, is the study of medicine, in which the earlier years of training are predominantly academic in spirit, and the later years, at any rate for the majority of medical students, predominantly technological A similar transition from the academic approach in the earlier years to the technological approach in the later years can be recognized in varying degrees in other vocational disciplines The complete segregation of such studies from more purely academic studies, because of their technological ending, would be most harmful for the general education of the students taking such mixed courses It would also leave even graver gaps than may arise at present in the university experience of students of the humanities Unless such ‘academic’ students become effectively aware of the technological activities of our contemporary civilization their education must be regarded as inadequate, and a failure so far as the university is concerned

Further strength is added to the educational objection against a complete segregation of technological from academic courses of study by the numerical importance of mixed or vocational studies in British universities

There is also a strong social objection to a complete separation of technologies from the universities It is well known that the supposed superiority of ‘black coated jobs’ over craft work has to some extent distorted school teaching in Britain Any stiffening of the social attitude in which the ‘university’ comes to be regarded as socially superior to the ‘technical college’ could be very harmful to the general welfare of the community, in deflecting potential students away from technological studies in which their real vocation lies

POSTGRADUATE INSTITUTES OF ADVANCED TECHNOLOGY

A reconciliation of the strong arguments for and against the segregation of technological studies from academic studies could be achieved by the creation or promotion of institutes of advanced technology, which would recruit students for higher technological studies either at the postgraduate stage or after they have been at least two years at a university For the more gifted technologists the total period of studies would be somewhat lengthened by this change

In some ways such a development would reflect experience in the teaching of medicine, but the detailed provision for advanced technological teaching would naturally vary with the main subjects envisaged Certain features can be recognized for such advanced training in the technologies, without going too far into hypothetical details What follows is necessarily somewhat tentative, and is advanced as a basis for discussion

Delicate and frequently controversial issues are raised by the problem of whether to aim at the creation of entirely new institutes of advanced technology, or whether to promote more extensive advanced work in selected technical teaching organizations already in existence Probably a combination of both policies would eventually prove most fruitful in promoting postgraduate work of the highest quality in technological studies

Allowance must be made for the fact that the existing technical bodies have a complicated teaching history They often fulfil an important need, which will quite possibly increase, in providing a training in a very wide range of crafts, including some scientific techniques, without requiring much more in the student than the immediate ability to learn the craft This important activity is quite irrelevant to and is frequently a distraction from any teaching for university degrees under para-university conditions

With the increased ease of access to universities there appear to be strong arguments that many of these para-university students should in fact be spending the early years of their postmatriculation studies at a university

Provided the students are of a type fitted for the academic approach, a university basis to their technological studies should be educationally of the greatest value Equivalent purely technological qualifications are generally available for students who are not suited for the academic approach, but who nevertheless can be trained into highly skilled craftsmen But a university degree should mean some exposure at some time to the university spirit

Such a transfer of the earlier years of higher technological studies to the university might free certain technical colleges for the task, which is often crowded out at present, of developing advanced and postgraduate teaching in the technologies But owing to the long historical background, such promotion would probably not lead to vigorous institutes of technology, in which the predominant emphasis is on postgraduate studies, in more than very few cases On the other hand the creation of new institutes of advanced technology cannot be lavish, owing to the cost of supporting selected students during the years of their postgraduate study, and owing to the very heavy administrative costs of experimental teaching in advanced technologies

On this basis one requirement for advanced technological work would come to be that the students must have a basic academic education in which some of the subjects studied would be determined by the subsequent vocational needs, but in which the methods of teaching would reflect the academic approach The educational argument for this broad foundation in highly trained technologists is strengthened by the consideration that during their active working life ready adaptation must be encouraged to any changes in the raw materials available for technological uses To take one example, the development of applications of plastics in engineering structures or of new fibres in textile technology can be an argument for including academic chemistry in the university training of engineers

If it is accepted that an institute of advanced or postgraduate technology must give really vigorous teaching in the methods of applying new knowledge, and must teach the experimental spirit in attempting new applications, it will immediately be apparent that various industrial firms are engaged in a parallel activity though in a narrower field Large firms often have training schemes to increase the experience and adaptability of their executives in special technologies But a link up of institutes of advanced technology with the activities of industrial firms is not likely to raise insuperable difficulties

The cost of a centralized teaching institute which has really adequate experimental facilities might be excessive if the heavier technologies are to be included on a footing wholly independent from the industry Effective teaching must normally be much more generalized than specific applications, and it seems likely that in practice an advanced teaching institute would feel the need for strong and possibly specific links not so much with the individual firms as with the research associations covering the same technological ground

ROLE OF RESEARCH ASSOCIATIONS

University experience provides abundant evidence that the interaction between advanced academic teaching and research is highly fruitful The notion that the research outlook is necessary for communicating the vitality of a science, as a growing body of knowledge, is so widespread that some experience of research is generally required even in teachers of elementary science in the universities In advanced technological teaching the ties with research would be expected to evolve differently in certain respects But the vitalizing function of research is quite as important and warrants careful consideration

Two important problems affecting the role of research in the advanced teaching of technology involve the growth of research associations and the combining of education in research methods with education in administration. The growth of research associations as organizations the scope of which is intermediate between the *ad hoc* day to day investigations required by industry and the academic pursuit of knowledge for its own sake has been very rapid in the last few decades. Although the body of factual knowledge which such associations can collect has proved to be of the greatest value for application in the industries concerned, it can be argued that until the higher training of advanced technologists is adequately linked up with the work of the appropriate research association, a very valuable educational byproduct of research is being wasted. In some cases the constitution and practice of the research association is still too fluid to permit a definitive assessment at the present time. But it seems worth while making a census of life histories of the research staff at least in the more long-established organizations. One object of such a census would be to determine what proportion of the research workers in a research association might be reasonably expected to take up technological posts in industry at a later stage. Such a sequence would help to spread the influence of background applied research in stimulating new technological developments. A second object of a census of staff in the research associations, which deserves careful assessment, is to determine how far the work of any of these associations could be linked up with advanced teaching of the technologies. A successful link up might bring benefits both to research and to the higher training of technologists. Having some advanced teaching to do could be a very valuable stimulus for selected research workers, since full time research for years on end is apt to produce a certain rigidity of approach. The tired research worker is even harder to fit into an active programme than the hackneyed teacher.

Another form of link up of the research activities proper to research associations with advanced teaching could be the taking in of students for a limited period of postgraduate work, say two or three years in research associations approved for this purpose. Such a suggestion must remain very tentative until the other principal teaching activities of an institute of advanced technology can be viewed as a whole. But the importance of promoting vigorous interaction between advanced teaching and research should be given proper attention before the practice and the functions of the research associations have become too fixed and crystallized.

TRAINING OF ADMINISTRATORS

It will be generally agreed that successful directors of research are born, not made. Similarly, administrators of the commercial side of an industry or of government offices cannot become adequately aware of the place of research in technological development, unless they start with the gifts of intelligence and character which are the basis of such awareness. However, natural gifts can be improved by education and enriched by instruction. In considering the future of higher education in the technologies we must examine how far such education develops administrative capacities. The most suitable form of university education for the future administrative classes of the community is still very much in dispute. Some vocational bias must probably be accepted even for students with this kind of future. And in our technological age it becomes urgent to decide how far and in what form to convey the technological approach to science, as distinct from the academic approach.

On the lines of the general argument developed above, higher technological studies would not become accessible to the most promising students until they obtained a primary degree or had spent at least two years in academic studies. More of the administrative classes of the future are likely to be chosen from students who have passed through a technological phase of studies and who have this broad academic foundation. Provided the universities do their job, such a development can be a welcome as well as a necessary outcome of the reorientation of higher studies to meet new demands. From all these considerations, higher education in advanced technologies calls for intensive review and judicious adaptation in the immediate future of Britain.

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Manurial Problems of Marginal Land

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LAND reclamation implies recovery from dereliction; the dereliction may be man made, that is it may have arisen from man's neglect or it may be the so-called natural state of the land. The end result is often similar, in that the land is dominated by a climatic or semi-climatic type of vegetation. This may take many different forms such as bracken, heather, *Nardus* or *Molinia* in the uplands, and thorn, birch or semi-aquatic types of vegetation in the lowlands, the last mentioned being more characteristic of low-lying fen or bog areas.

In many respects the way in which dereliction occurs may be of little importance to the reclaimer; on the other hand it may have a very important bearing on the manuring and cropping procedure which should be adopted. A considerable amount of information on these problems was gathered during the 1939–45 war. As SIR GEORGE STAPLEDON once aptly remarked, it was becoming increasingly important to distinguish between land to be reclaimed which had some known agricultural history and that which had no known agricultural history.

BRACKEN AREAS

In mid-Wales as well as in western and northern England, large areas of this latter type were brought under the plough in order to increase the home grown food production drive. The work carried out at the Cahn Hill Improvement Station near Aberystwyth between 1934 and 1939 had provided much basic knowledge relating to certain aspects of the mechanical and technical problems encountered in reclaiming land of this nature. Most of this information, however, related to land which was being improved to provide better grass rather than crops, especially such crops as potatoes. Another important factor which should be noted is that much of the early wartime work was carried out in an atmosphere of speed and urgency with the result that many examples were encountered which amply justified the proverb 'more haste, less speed'.

POTATOES IN BRACKEN AREA

One such instance was an attempt to grow potatoes on a newly ploughed bracken area 1,200 ft (c. 350 m) above sea level. Soil analyses had shown that the *p*H varied from 3.7 to 4.3, the phosphate deficiency was equivalent to 80 to 100 lb/acre (c. 90–110 kg/ha) phosphorus pentoxide P_2O_5, but there was a natural reserve of potash sufficient to grow at least one crop of potatoes. The country's plight necessitated the application of every effort to produce human food crops as quickly as possible. Consequently this particular area was planted with potatoes within nine months of its being ploughed for the first time, without being 'pioneer' cropped in any way with such crops as rape and turnips which had been found to be best at the Cahn Hill Improvement Station. The technique of pioneer cropping will be discussed more fully on p. 60.

One disadvantage of growing potatoes in this way was that the deep cultivations required were seriously obstructed by the presence of undecomposed bracken roots. This difficulty was even more serious when the land was being thrown up into ridges prior to planting and when the ridges were to be split to cover the tubers. Much extra time and patience were required to carry out these operations reasonably efficiently. Through lack of supplies only part of the area could be given a dressing of 30 cwt/acre (3.8 tonne/ha) of calcium carbonate; the remainder was left unlimed. At planting time, a complete potato fertilizer equivalent to 78 lb/acre (87 kg/ha) nitrogen, 78 lb/acre (87 kg/ha) phosphorus pentoxide and 56 lb/acre (63 kg/ha) potassium oxide was applied to almost the whole area. In this compound the nitrogen and phosphates were in the form of ammonium phosphate. Because there were certain misgivings about the wisdom of planting the potatoes on this land without lime and with this type of fertilizer it was decided to manure part of the unlimed area with an equivalent dressing of nitrogen, phosphorus and potassium, but using basic slag as the source of phosphate. The plants on the limed and slagged areas grew normally and always had a good healthy appearance while those which received the complete fertilizer only were much slower in coming through the ground and subsequently made very poor growth. Their general appearance was small and stunted with a pale yellow green colour; the stems were rigid and wiry. On a sunny windy day the leaves curled up, giving the impression that the crop was suffering from a severe attack of leaf roll. When the parent tubers were examined they were generally found to be quite hard and firm, and not soft or shrunken or in any way decomposed as parent tubers are generally found to be after the new plant has been above ground for some weeks. A number of these hard tubers were removed and replanted in a good lowland soil, where they gave rise to normal healthy plants.

EFFECT OF FERTILIZERS

The manurial experiment was later carried out on a randomized plot basis and gave the same general results Yield data were collected and if the yield of the fertilized but unlimed plot is put at 100 which is approximately equal to a yield of 1 ton/acre (2·5 tonne/ha) the results might be briefly summarized as in *Table 1* The composition of the complete fertilizer is 14 per cent nitrogen, 14 per cent phosphorus pentoxide 10 per cent potassium oxide

Table I Response to Various Manurial Treatments

Plot No	*Addition*	*Relative Yield*
1	*5 cwt (250 kg) complete fertilizer* *No lime*	100
2	*5 cwt (250 kg) complete fertilizer* *30 cwt (1·5 tonne) ground limestone*	1,000
3	*30 cwt (1·5 tonne) ground limestone* *No fertilizer*	500
4	*3·3 cwt (170 kg) ammonium sulphate* *4·6 cwt (235 kg) 15 per cent basic slag* *1 cwt (50 kg) 50 per cent potassium chloride* *5 cwt (250 kg) complete fertilizer* *No lime*	1,100
5	*As 4 but with 18 per cent superphosphate instead of 15 per cent basic slag*	650

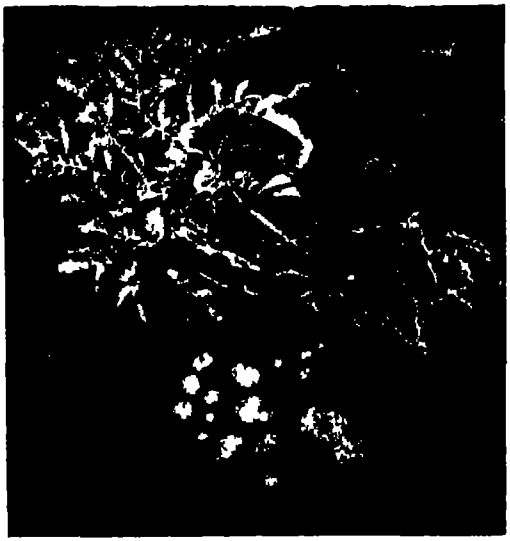
A parallel series of plots was laid out under the direction and guidance of R O Davies, then Advisory Soil Chemist at Aberystwyth Chemical analyses were made of the leaves and stems of plants growing on the variously manured plots similar to those shown above The results of this work have been published by R O Davies, I W Lacan and J L John[1] and show that the leaves and stems of the potatoes grown on unlimed or unslagged areas were exceptionally low in both calcium and phosphoric acid Plants grown on the plots which received either ground limestone or basic slag showed a fourfold increase in the calcium content of the stems and leaves This was accompanied by a marked increase in their phosphoric acid content

IMPORTANCE OF CALCIUM

The indication, therefore, is that calcium was a primary limiting factor in the growth and development of the potato plant There was insufficient available calcium in the natural soil to provide an adequate supply of calcium as a plant food, which in addition brought about either excessive reversion of the soluble phosphoric acid in the soil and/or the lack of an adequate supply of a suitable base for the uptake of phosphoric acid by the plant The low *p*H of the soil in itself appears to be a minor factor so far as the potato crop is concerned, since there seems to have been a sufficient supply of calcium in the basic slag to act as a plant food and a base for phosphoric acid uptake, but not enough to materially affect the *p*H value of the soil

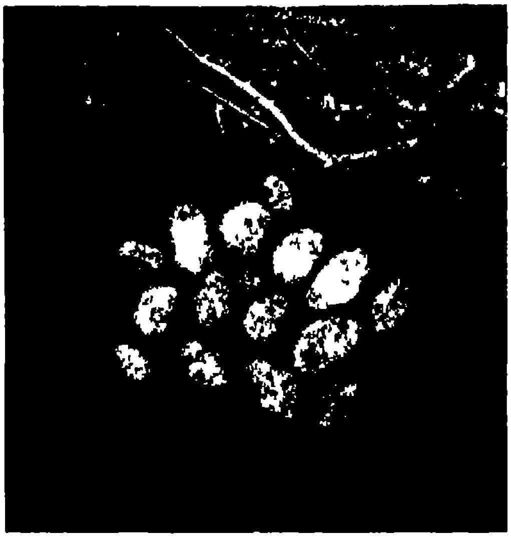
Further evidence in support of this explanation was obtained later, when by substituting nitro-chalk for sulphate of ammonia on the plots receiving superphosphate an increased yield was obtained Conversely an increase in the amount of ammonium sulphate on the similar plots actually decreased the yield, presumably by reducing the amount of calcium available to the crop as a plant food or a phosphate base T Wallace and E J Hewitt[2] have investigated the phenomenon of the parent tuber remaining hard and firm and have concluded that it is entirely due to the deficiency of available calcium *Figures 1* and *2* show the produce and the leaves and stems of plants grown on areas receiving a complete ammonium phosphate fertilizer only, and complete fertilizer dressing containing basic slag, respectively Subsequent to and partly as a result of these experiences a policy of pioneer cropping was adopted on other areas that were reclaimed later Such areas were usually dominated by either *Nardus Nardus*-fescue, *Molinia*, heather or bracken The analyses of these soils varied slightly but in general terms showed deficiencies similar to those for the bracken area mentioned above, namely 25 to 35 cwt (1,250 to 1,750 kg) of calcium oxide and 80 to 100 lb (36 to 45 kg) of phosphorus pentoxide and except on the bracken areas a deficiency equivalent to 30 to 50 lb (13·5 to 22·5 kg) of potassium oxide

Every effort was made to apply lime as soon as possible after ploughing and generally phosphorus pentoxide and potassium oxide as advised by the soil chemist immediately before sowing the crop One to two cwt/acre of sulphate of ammonia was also applied at sowing time or soon afterwards The purpose of the pioneer crop is to obtain produce which will have a manurial value either through being ploughed in as a green manure or after being eaten off by stock The latter is to be preferred since the treading of the animals, whether sheep or cattle, is valuable in helping to break down the old turf or buried vegetation as well as the fibrous roots in the soil, especially bracken roots It is also generally accepted that the dunging and urinating by the stock is important in restoring and raising the general fertility level of soil Used in this sense the term fertility covers all the complex aspects of soil life—bacteria and other micro-organisms as well as the chemical attributes of the soil—all of which are necessary to enable a soil to be reasonably productive



Courtesy Royal Agricultural Society and 'Farming'

Figure 1 Produce, leaves and stems of plants grown on areas which received complete fertilizer, ammonium phosphate type, at the rate of 5 cwt/acre (630 kg/ha) but no lime



Courtesy Royal Agricultural Society and 'Farming'

Figure 2 Produce leaves and stems of plants grown on areas which received a dressing of complete fertilizer mixture at the same rate as in Figure 1 The phosphate was supplied in the form of basic slag No lime was given

so far as the plants demanding higher fertility are concerned This, of course, from the point of view of reclamation is of vital importance, since the land must be made capable of growing plants or crops of real value either as stock or human food Prior to reclamation the production was of relatively little value even to the grazing animal There seems to be need for further research into problems relating to the aspects of bacteria and micro-organisms in virgin soils of these types The rectification of chemical deficiencies is undoubtedly the first step, but the matter does not end there

PIONEER CROPS

The crops generally used as pioneer crops are rape, turnips, swedes, kales, Italian and perennial ryegrass, winter or spring rye or some other cereal These may be used separately or in mixtures The brassica crops normally have the advantage of giving a greater yield per acre than the gramineous species, especially if sown fairly early in the summer Furthermore if gramineous species are included with a crop of brassicae, which grows successfully, they are generally smothered out Consequently they are only included in the mixture when there is some doubt about the chances of the brassica crop being successful or where it is sown thinly for some other practical reason

The general experience with brassica crops in mid-Wales on upland virgin reclaimed areas was that certain prerequisites were necessary to ensure reasonably good results These were

1 the land should have been ploughed and adequately limed at least about six months before the crop was to be sown ,
2 the lime, particularly ground limestone should be reasonably finely divided preferably so that 60 per cent or more would pass through the 100 mesh sieve in order to obtain more even distribution and a quicker effect in the soil Other evidence indicates that fineness of grinding is of minor importance on lime-deficient land which is being farmed in the ordinary way ,
3 the crop should be given adequate dressings of nitrogen, phosphorus and potassium (N P K)

Rape, turnips and kales were either partial or complete crop failures, *Figure 3*, when grown on land which had not been ploughed more than a few weeks or to which lime in any form had not been applied until relatively near the time of sowing Similar results were obtained when coarsely ground (40 per cent) limestone was used even four months prior to sowing Analyses of these brassica plants showed a deficiency of calcium and phosphoric acid similar to that seen in the case of the potato crop Disease in the form of 'finger and toe' or 'club root' was not encountered in any of these instances A further interesting experience with a brassica mixture was

Figure 3 Rape grown on reclaimed virgin land after a dressing of 2 ton/acre (5 tonne/ha) of coarsely ground limestone applied 2 months before sowing 5 cwt/acre (630 kg/ha) of a compound fertilizer ammonium phosphate type, was applied at the time of sowing

noted on an area of about 60 acres (24 ha) all of which had received 30 cwt of ground limestone per acre (3 8 tonne/ha) several months before the crop was sown One part received a dressing of 5 cwt/acre (630 kg/ha) of complete fertilizer (N P K) with the nitrogen and phosphate present as ammonium phosphate The remainder was given a similar dressing of N P K using sulphate of ammonia and basic slag to supply the nitrogen and phosphorus pentoxide When sheep were turned in they ranged over the whole area before settling down on that part which had been given the basic slag This they grazed relatively bare before going on to the area where ammonium phosphate has been used as a constituent in the complete fertilizer There was no marked visible difference between the crops before grazing commenced Unfortunately it was not possible to follow up or repeat this experiment or to formulate any precise explanation for the behaviour of the sheep

In many of the brassica mixtures Italian ryegrass was included at the rate of 15 lb/acre (17 kg/ha) as an insurance crop In practically all instances where the brassica crop was a partial or complete failure for one of the reasons given above, but where lime and complete fertilizer had been applied, the Italian ryegrass grew successfully The same can be said of perennial ryegrass and rye, especially winter rye Experience therefore showed that these members of the gramineae were better suited for use as pioneer crops than members of the brassica family, especially where the lime had not been given time to function or become thoroughly mixed in the soil Such results are not surprising in view of the lime-loving nature of most brassica farm crops, and this knowledge avoided many disappointments at a later stage Brassica crops generally give much better results on exhausted farmed lands in less need of fertility rehabilitation than such virgin lands as were dealt with in this work

Even Italian ryegrass and rye were, however, almost complete failures when grown on areas that received only a complete fertilizer (ammonium phosphate type) and no lime Analyses of the leaves revealed calcium and phosphoric acid deficiencies similar to those mentioned above Plants growing under these conditions are illustrated in *Figure 4*

Pioneer crops of all kinds were often partial failures when grown on some of the heavier types of soil, especially those reclaimed from *Molinia*, heather or the wetter *Nardus* areas, even when sufficient lime, phosphate and potash had been applied in the right manner The initial establishment was generally satisfactory but subsequent growth of the plants was poor and stunted Such plants ultimately developed the purplish and yellowish colorations that are associated with phosphate and nitrogen deficiencies

During the war years it was impossible to have any determination made of the status of the soil in terms of the activity of bacteria or other microorganisms The crops had been given a dressing of 1 to 2 cwt (50 to 100 kg) of sulphate of ammonia at the time of sowing As a trial, selected areas were given an extra 2 cwt (100 kg) of sulphate of ammonia This brought about a marked improvement Similar results were obtained on grasses such as perennial ryegrass, timothy and cocksfoot where direct reseeding was carried out In the absence of more precise information it would seem that on some of these soils the numbers and activity of the

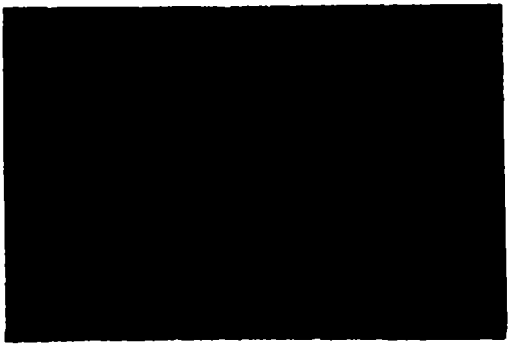


Figure 4 Poor crop of a mixture of winter rye and Italian ryegrass grown on part of an area which received only 5 cwt/acre (630 kg/ha) complete fertilizer and no lime

soil bacteria and other useful micro-organisms is so low that it becomes a limiting factor in the growth of the higher fertility demanding crops. It would also appear that this can best and most quickly be overcome by giving a more generous supply of artificial nitrogen to the first crop. This is substantiated by experience in New Zealand where in their upland areas lime and phosphate are essential for the initial successful establishment of the clovers. Through the clovers there is an accumulation of nitrogen in the soil which is essential in enabling the grasses to become fully established and completely productive.

In the same connection the work of F C GERRETSEN which is quoted by F HANLEY[3] is interesting. According to this report the activity of soil micro-organisms increased the uptake of phosphates by the roots of the plants situated in their immediate neighbourhood.

CLOVER CROPS

Clovers themselves are, of course, dependent on special strains of bacteria for their successful establishment, and like the brassica crops are sensitive to low *p*H values. On these soils in the earlier years of cropping broad red clover was found to be difficult to establish and general growth was poor, late flowering types were more successful, but alsike was better than either form of red clover. White clover, however, gave the best results and almost invariably a good seedling stand was obtained. Even with this species it was found that subsequent growth and establishment were often uncertain, depending on the calcium and phosphate status of the soil. This was clearly illustrated on one area where no lime but ½ ton/acre (1.3 tonne/ha) of basic slag together with 1½ cwt/acre (190 kg/ha) of sulphate of ammonia were applied. The clovers, alsike and white clover, germinated and grew well until the four leaved stage was reached after which practically all the plants developed reddish to yellow coloration in the leaves and died off relatively quickly. This was probably partly due to the low *p*H and the low calcium status of the soil, but may also have been caused by the lack of molybdenum which according to E J HEWITT[4] is essential for the effective activity of the symbiotic bacteria of clovers.

Even in areas where adequate dressings of lime and phosphates were applied the development of white clover after the seedling stage was often weak and poor. Examination of the roots of these plants showed that the nodules were very small compared with those on similar plants on better land. After the first year, however, these plants improved in strength and vigour and nodulation appeared to be fairly normal. Hewitt[4] believes that under such conditions sufficient molybdenum is liberated through the effect of the lime to meet the requirements of the symbiotic bacteria.

On one area innoculated white clover seed was used. The seed was sown in the spring (early May) in a grass seed mixture. Counts taken in the late summer (September) showed that there were nearly twice as many plants per unit area where innoculated seed was used compared with that where non-innoculated seed was sown. By the following summer, however, there was very little difference between the two areas in terms of the percentage ground covered by the white clover indicating that innoculation with the appropriate strain of bacteria was not, as such, a limiting factor in the successful establishment and development of white clover under these conditions.

The efficacy of these bacteria appears to be dependent on the presence of an available minor element as indicated above.

CONCLUSIONS

In general terms the results of these experiences would seem to indicate that in dealing with relatively virgin land of this kind, land without a known positive agricultural history, it is essential to rectify the major mineral deficiencies as a first step. In addition, however, there are other factors to be considered, such as minor elements, soil bacteria and other micro-organisms about which much still remains to be known. As with the importance of molybdenum to the symbiotic bacteria of the clovers, the answers to many of these problems will be found through further research work.

In the meantime the farmer and the husbandryman must continue evolving ways and means of overcoming the difficulties in the field without always knowing exactly why what is being done by them is effective.

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Chemistry of Lignin

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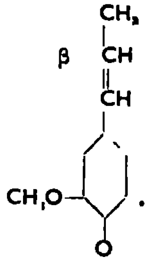
FROM 1890 and for the rest of his long life PETER KLASON, the grand old man of lignin chemistry, held the view that spruce lignin is related to coniferyl alcohol A massive amount of evidence collected by K FREUDENBERG, H HIBBERT, B HOLMBERG and others, points in the same direction and shows that the C_6C_3 units are joined by ether linkages At intervals, however, the aromatic nature of lignin has been questioned by various authors

Studies of the ultraviolet absorption of products obtained on stepwise sulphonation of low sulphonated lignin sulphonic acids and especially of untreated wood recently carried out by G AULIN-ERDTMAN *et alii*[1] and by P LANGE[2], respectively, have completely and definitely disproved the view that lignin is not aromatic

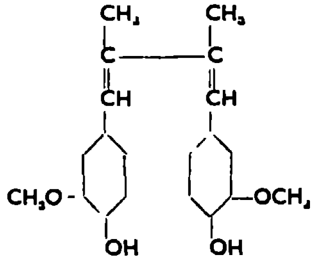
During my years in Sir ROBERT ROBINSON'S laboratories I studied the dehydrogenation of phenols, which proceeds with formation of diphenols or phenol ethers The couplings to the hydroxyl group take place in the *o* or *p* positions I tried to extend these dehydrogenations to phenols which have a side chain containing a double bond conjugated with the nucleus and situated in one of these positions They should be capable of coupling at the β carbon atom of the side chain[3-5] My intention with these experiments was to try to throw light on the biogenesis of the group of naturally occurring compounds[6] later termed lignans by R D HAWORTH

The dehydrogenation of *iso*eugenol to a coupled crystalline product had already been accomplished by H COUSIN and H HÉRISSEY[7] In spite of the fact that the methyl ether on oxidation furnished veratric acid H HÉRISSEY and G DOBY concluded that ' dehydrodi-*iso*eugenol ' was a diphenyl derivative similar to dehydrodi-vanillin[8] I first believed that dehydrodi-*iso*eugenol was dehydro-guaiaretic acid *II* formed from *I* by coupling at the β carbon atoms[6]

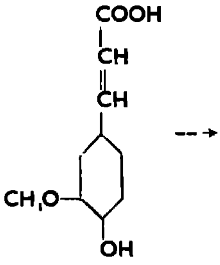
Ferulic acid *III* yielded a dehydrodi-ferulic acid, recognized as a dilactone for which structure *V* was provisionally suggested The yield was small and the structure was never proved Nine years later this was done independently in an elegant way by N J CARTWRIGHT and R D HAWORTH[9] R D HAWORTH also points out that the lignans may owe their formation in Nature to a side chain dehydrogenation of similar phenols[10]



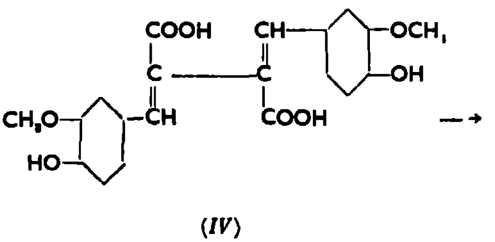
(*I*)
Isoeugenol—(H + *e*) *showing reactive positions* ( )



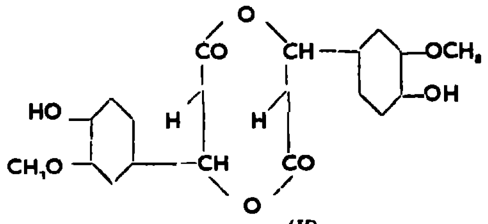
(*II*)
' *Dehydro-guaiaretic acid* '



(*III*)
Ferulic acid

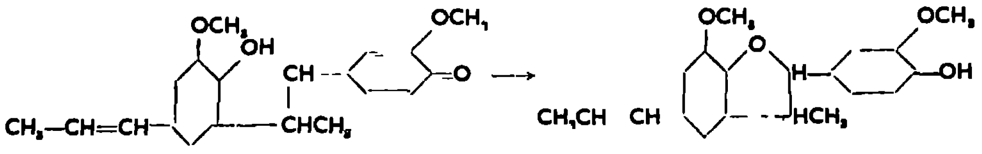


(*IV*)



(*V*)
Dehydrodi-ferulic acid

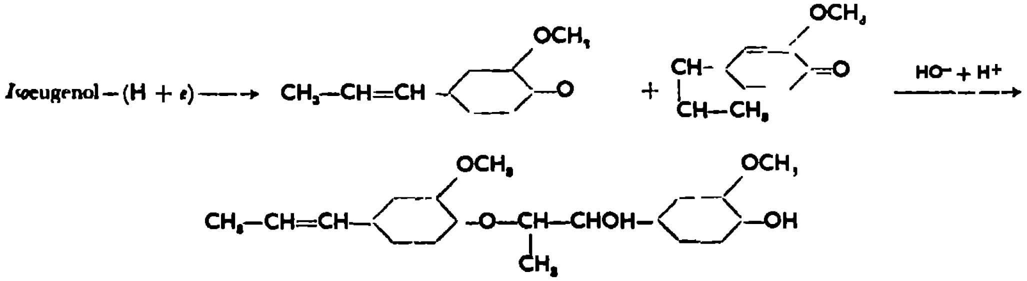
Further studies on the dehydrodi-*iso*eugenol disproved the views of Herissey and Doby as well as structure *II*. Coupling, obviously, takes place between the *o* position in one molecule of *iso*eugenol and the β carbon atom of the side chain of another followed by the formation of a coumaran derivative[3,4], *VI-VII*.



(*VI*) (*VII*)

This structure *VII* is similar to structural schemes for lignin proposed at that time by K. FREUDENBERG without referring to any mechanism involving dehydrogenation[11]. Since the reaction clearly could be imagined to proceed indefinitely by further dehydrogenations and additions of new *iso*eugenol residues I advanced in 1933 the hypothesis that lignin is formed in Nature by dehydrogenation of C_6C_3 progenitors of the coniferyl type[4]. The mechanism which I proposed would easily explain why no optical activity has been observed in any lignin derivatives. Subsequently similar views have been expressed by K. FREUDENBERG and his collaborators and are now apparently in fashion among lignin chemists[12-14].

In the last fifteen years I have made many attempts to accomplish the following reaction which would be of great interest to lignin chemistry:



(*VIII*)

With *iso*eugenol and several analogous compounds, however, invariably ill defined, amorphous products were obtained similar to the dehydrogenation products described by Freudenberg[14].

SULPHONATION OF LIGNIN

The most important reaction of lignin is its sulphonation with sulphites, which affords lignin sulphonic acids. The pioneer work of E. HAGGLUND shows that this proceeds in two steps[17].

In the first step a 'sulphonated wood' containing an insoluble lignin sulphonic acid is obtained. This cannot be removed by simple washing with water. As Hagglund has shown, boiling with acids or suitable buffer solutions is needed to accomplish solution. The 'solid insoluble lignin sulphonic acid' of Hagglund is formed more rapidly if the cooking liquor is acid than if it is neutral. It is, however, also formed with sodium sulphite in slightly alkaline solution. With an acid cooking liquor a more highly sulphonated solid lignin sulphonic acid is formed but simultaneously great losses of lignin occur due to formation of soluble lignin sulphonic acids.

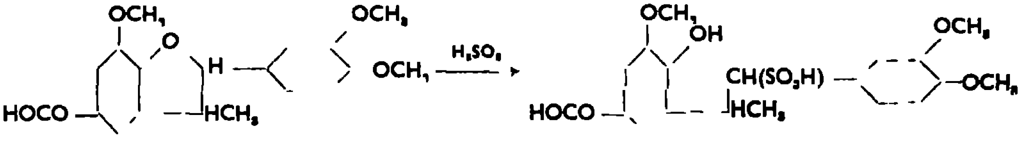
In the second step the solid lignin sulphonic acids are transformed into soluble acids. Hagglund believed that this step was essentially a hydrolysis of bonds between the partly sulphonated lignin molecules and carbohydrates (or between several smaller lignin molecules, 'depolymerization'). This step normally appears to be accomplished by an additional sulphonation. In normal acid pulping these steps may overlap, but the second step predominates in the later phases of the pulping process when the cooking liquor becomes more acid due to withdrawal of calcium ions (formation of sulphonic acid salts).

Turning now to the chemistry of the process, the fundamental experiments of Hägglund suggest the presence of two different reactive groups in genuine lignin. One group, here called A, is more or less readily sulphonated over the whole *p*H range. Another group B is sulphonated easily only in the more acidic *milieu* prevailing at the end of the cook. It is immediately apparent that this group B very probably is identical with the group which is hydrolysed in step 2

Hägglund has shown that sulphonation of wood with a strongly buffering sulphite solution of *p*H 6 rapidly furnishes a wood residue containing lignin sulphonated to an extent of one sulphonic acid group per 3 5 to 4 C_6C_3 units Further sulphonation proceeds only very slowly as also does delignification

Sulphonation of wood at a lower *p*H rapidly furnishes a wood residue containing a more highly sulphonated lignin, up to one sulphonic acid group per two C_6C_3 units This is about the same sulphur content as that of soluble lignin sulphonic acids from technical waste liquors

In the first instance apparently only the groups A are sulphonated In the second all groups A are sulphonated and part of the groups B are hydrolysed and sulphonated When the last group B in one molecule is cleaved the lignin sulphonic acid looses contact with the carbohydrates (or the complete depolymerization of the genuine lignin is *accomplished*) and the now soluble lignin sulphonic acid passes into solution



(*VI*) (*VII*)

C Kullgren[18] has shown that 'strong sulphite pulp' which is a sort of sulphonated wood acts like a cation exchanger Charged with hydrogen ions and heated with distilled water this material looses lignin sulphonic acids This is obviously due to the hydrolysis of residual B groups

There is also other evidence indicating the actual presence of two groups of different reactivity in genuine lignin In Hagglund's laboratories I found in 1940 that wood is readily sulphonated in the presence of reactive phenols (resorcinol, pinosylvin) under neutral or only weakly acid conditions[19] If the acidity is subsequently increased a normal delignification occurs If, however, wood is sulphonated with strongly acid cooking liquor in the presence of reactive phenols the lignin preferentially reacts with the phenols to yield a product similar to bakelite which contains sulphonic acid groups

This is easily explained by assuming that it is the groups A that react with phenols in the presence of acids but that these groups do not react with phenols under more neutral conditions The groups B do not react with phenols at any normal *p*H but are hydrolysed and sulphonated by acid cooking liquor The result is a sulphonated insoluble lignin-phenol condensation product

REACTIVE GROUPS IN LIGNIN

What is the chemical nature of these groups A and B? This fundamental question has been subjected to much speculation Omitting less probable hypotheses it is sufficient to mention two conflicting ideas both supported by model experiments

B Holmberg *et alii*[20-22] suggested that sulphonation involves the substitution of a hydroxyl group possessing outstanding reactivity He believed this to be of the benzyl alcohol type and found a useful model in *α*-phenethyl alcohol

$$\underset{(IX)}{C_6H_5\text{—}CH(OH)\text{—}CH_3} \xrightarrow{H_2SO_3} \underset{(X)}{C_6H_5\text{—}CH(SO_3H)\text{—}CH_3}$$

Not denying this possibility K Freudenberg[23] advocated the view that a heterocyclic ring similar to that in dehydrodi-*iso*eugenol is cleaved with formation of a phenolic sulphonic acid

Both reactions, however, proceeded more slowly than the sulphonation of lignin and none of these authors discusses the two reactive groups in lignin, the presence of which I believe, must be assumed

It remained to be investigated whether the sulphonation of lignin is accomplished by the disappearance or formation of hydroxyl groups

K Freudenberg, W Lautsch and G Piazolo attacked this problem in an elegant way[1] They pulped wood fractionally at a low temperature and obtained a series of sulphonated acids of increasing sulphur content The free acids were dried at 55°C and the hydroxyl content determined by acetylation experiments Contrary to expectation the more highly sulphonated acids did not contain more hydroxyl groups than the less sulphonated ones The experimental procedures employed, however, were such that the authors hesitated to draw definite conclusions It was obvious, however, at least that in this mild sulphite cook no phenolic hydroxyl groups were formed

Recently, however, K Freudenberg and G Dietrich maintained that the fission of ether linkages as in *XI*→*XII* must be assumed on account of the fact that neither lignin nor methylated lignin yields *iso*hemipinic acid on oxidation, whereas *iso*hemipinic acid was obtained in small yield from methylated lignin sulphonic acids It appears however, to be quite possible that the formation of *iso*hemipinic acid is due to a secondary condensation reaction taking place during the sulphite cook One convenient method for preparing *iso*hemipinic acid is due to a condensation such as

$$\text{eugenol} \xrightarrow{\text{formaldehyde}} \text{'eugenotin alcohol'} \xrightarrow{\text{methylation oxidation}} \textit{iso}\text{hemipinic acid}^{7}$$

Formaldehyde is produced from lignin when heated with acids or alkali[8]

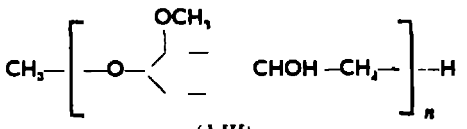
In order to throw light on this problem low sulphonated lignin sulphonic acids obtained from sulphonated wood were prepared according to Kullgren's procedure With B LINDGREN and I PETTERSON it was shown that the stepwise sulphonation of such acids was accompanied by the equivalent loss of hydroxyl groups[9]

The technique employed was the acetylation of the pyridine salts of the various sulphonic acids with acetic anhydride in pyridine isolation and complete analysis of the products obtained Spectrochemical investigation of the low sulphonated acids and their sulphonation products in neutral and alkaline solution establishes that no phenolic hydroxyl groups are formed during this sulphonation process[10]

MECHANISM OF SULPHONATION

These results strongly indicate that lignin sulphonation is mainly due to substitution of hydroxyl groups The low sulphonated lignin sulphonic acid employed contained sulphonic acid groups corresponding to part of the groups A The groups B were cleaved by hydrolysis during the Kullgren process but remained capable of sulphonation

The groups A reacting with sulphite at all *p*H values but with phenols only at a low *p*H are believed to be of the benzyl alcohol type Assuming this B LINDGREN studied the reactivity of similar alcohols of a more lignin-like structure[11] He found that for example vanillyl alcohol, veratryl alcohol and their homologues are sulphonated very readily Indeed they react more readily than lignin, which is probably due to their solubility In fact they tally in their reactivity in almost every respect with the groups A in lignin They are for example sulphonated in the presence of phenols with neutral cooking liquor but they condense under more acid conditions The groups A are believed to belong, essentially, to elements of the type *VIII* With B LEOPOLD a series of compounds of similar type, *XIII*, has been synthesized[8]

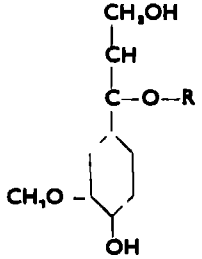


(*XIII*)

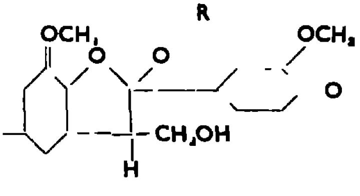
where *n* = 2 to 4 These substances were easily sulphonated and also in other respects behaved as if they contained the A groups of lignin

Group B is obviously an acetal group Since B is apparently hydrolysable to a group B′ containing a hydroxyl group capable of being substituted by a sulphonic acid group, it is presumably a *cyclo*-acetal group and B′ a cyclic semi-acetal group

Formula *XV* illustrates this hypothesis, the element could be formed from *XIV* (R = a polysaccharide chain or a lignin chain) by dehydrogenation in exactly the same way as dehydrodi-*iso*eugenol This also applies to the formation of *XV*

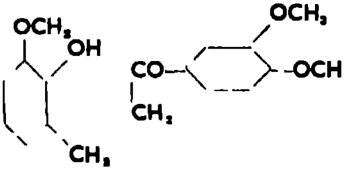


(*XIV*)

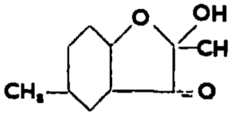


(*XV*)

Good model substances are not easily available Hitherto we have studied the following[1]



(*XVI*)



(*XVII*)

The hydrogenated chalcone *XVI* does not furnish a cyclic semi-acetal and cannot be sulphonated. Compound *XVII* yields a sulphonic acid (OH → SO_3H) which has been resolved into optically active forms and found to be remarkably stable with alkalis and acids. The carbonyl group may here facilitate the exchange reaction OH → SO_3H and the substance is not regarded as being a particularly good lignin model. The studies of these substances are being continued.

If the Kullgren process is carried out in ethanol instead of water, ethoxyls containing low sulphonated lignin sulphonic acids are obtained[18]. On further sulphonation the ethoxyl groups are split off as alcohol and sulphonic acid groups are then introduced[33].

This recalls early experiments on the ethanolysis of wood by B Holmberg and S Runius, who also recognized carbonyl functions in lignin[34]. In *XV* these functions are 'masked'.

The assumption that lignin is to a large extent built up from groups of the types *VIII* and *XV* is in agreement with analytical results of Holmberg and Freudenberg. They point to an average composition of $[C_9H_9O_3(OCH_3)]_n$. Type *VIII* possesses that composition but type *XV* has two hydrogen atoms less.

The exact determination of hydrogen in amorphous preparations is difficult. A mixture of $C_9H_9O_3(OCH_3)$ and $C_9H_7O_3(OCH_3)$ element may well give analytical results agreeing with the formula for composition given above.

There are necessarily some elements in lignin which possess a somewhat modified structure. The methoxyl content is a little too low, some free aldehyde groups are obviously present and spectrochemical evidence conclusively shows that there must be some elements possessing larger conjugated systems[8], perhaps phenylcoumarones from element *XV*.

Much work remains to be done and this is only intended to be an attempt to look upon the chemistry of lignin, especially its formation in Nature and its sulphonation, from a somewhat idealized point of view.

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Powerful Acoustic Waves

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PHYSICAL aspects of the propagation of sound waves *i e* mechanical vibrations, have been the subject of detailed study for over a century Within the last thirty years it has been found that very intense acoustic waves produce unexpected physical, biological and chemical effects in the medium through which they pass The production of these effects requires sources dissipating tens if not hundreds of watts and these are of an entirely different type from those encountered in acoustics where a sound with a small fraction of a watt of energy is a most intense noise

The use of sound waves—usually of high frequency—in the fields of underwater communication (including submarine detection and echo depth sounding), testing of materials *e g* flaws in metal castings, and in the Scophony system of television is beyond the scope of this article, which confines itself to the chemical and physical effects produced in solids and liquids by very intense sound waves

Mechanical vibrations are usually divided into two categories according to frequency, oscillations with frequencies less than 10-20 kc/s are known as sonics and those with greater frequencies as ultrasonics In the past the terms 'ultrasonic' and 'supersonic' have been used indiscriminately and this has lately led to considerable confusion because of the wide use of the term 'supersonic' to describe motion at a speed greater than that of sound The writer urges that the term 'supersonic' be confined to this use and that sound waves with frequencies beyond the audible be called 'ultrasonics'

The average adult is in general not able to hear sound of frequency greater than 12 kc/s although this varies from person to person, but the writer has found that intense sound waves right up to 25 kc/s are capable of being detected even though they do not produce a sensation of sound but rather some indeterminate and unpleasant feeling that something is happening The term 'sound' will in this article be used for all mechanical vibrations, whether of sonic or ultrasonic frequency

In their physical and chemical effects there is no dividing line between sonics and ultrasonics, and it is very doubtful whether any of the effects produced are frequency dependent For experimental reasons most of the oscillators built for producing intense mechanical vibrations for research purposes operated in the ultrasonic frequency range and until recently few experiments were carried out with powerful sonic generators This is undoubtedly the reason for the frequent indiscriminate use of the term ultrasonics for all high intensity mechanical vibrations The frequency limits for high intensity sound waves are set by the practical difficulties of producing high energy content oscillations The energy of a sound wave is, of course, a function of frequency and amplitude and hence it becomes very difficult to obtain high intensities at less than 5–8 kc/s as it is impossible to obtain the necessary amplitude in mechanical systems The upper limit of frequency for power sources is at about 3 Mc/s for design reasons which will be discussed in the next section

Very many strange phenomena have been observed with powerful sound waves but they are always attributable to one or more of the four chief effects associated with energetic vibrations These are production of heat, radiation pressure, cavitation in liquids, and the enormous acceleration of particles in the sound beam leading among other things to an increase in the rate of diffusion through membranes Some of the many different effects obtained such as emulsification, sterilization and grain size reduction during crystallization have great potential value and will find industrial outlets as soon as a cheap method of producing high intensity sound waves is found

SONIC AND ULTRASONIC GENERATORS

Piezoelectric oscillator— This type of generator is the one most frequently used for experimental work with ultrasonics and is the only type of generator capable of working satisfactorily at frequencies above 100 kc/s The brothers J and P CURIE discovered in 1880 that a number of crystals such as quartz, tourmaline, Rochelle salt, zinc blende and cane sugar produced electrical charges on their surfaces when subjected to mechanical pressure Later investigations showed that this effect is common to all crystals which do not possess a centre of symmetry The underlying theory has been worked out in detail but cannot be discussed here The converse effect, namely that the application of an electric field of force produces a contraction or expansion of the crystal, was predicted from thermodynamic considerations and later experimentally confirmed by the Curies

The basis of the piezoelectric ultrasonic generator was laid by M P LANGEVIN and the first powerful generators were built by R W WOOD and A L LOOMIS who, like all subsequent experimenters, used

quartz crystals as the piezoelectric material The basic principle is to apply to the crystal an alternating current at very high voltage and at the same frequency as the natural elastic frequency of the crystal in the appropriate direction In this way, powerful mechanical oscillations are set up from the surface of the crystal Usually, the crystal is cut into plates of which the thickness governs the resonance frequency at which they oscillate The thickness of a crystal resonant at 300 kc/s is 1 cm and at 3 Mc/s, 1 mm It can readily be seen that it is the thickness which effectively limits the frequency range, as very big crystals are difficult to find and very thin crystals too fragile to handle The crystallographic aspects of cutting the crystals are well understood and lens shaped crystals can be made which focus sound waves, making possible very high local intensities A beam of sound waves can also be focused even when emitted from a flat crystal by using a mirror in exactly the same way as a parallel beam of light If the sound waves are in a liquid any solid *e g* glass can be used as a mirror, but losses are inevitable since no solid acts as a perfect reflector for sound at a liquid interphase

Until recently, a Tesla coil was employed to couple the high frequency oscillator to the crystal for the conversion of electrical to mechanical energy The design of the coupling circuits was largely empirical and the method always very inefficient since great heat losses occur in the coil Probably the most efficient coupling method utilizes a Π network, and a generator working on this principle has been described in detail in a most valuable paper[1] The mechanical properties of quartz limit the frequency range from 50 to 2,000 kc/s for high power oscillators The overall efficiency of a quartz oscillator in the conversion of electricity to sound has been variously estimated from 10–70 per cent but probably lies in the region of 20 30 per cent for the best machines This efficiency, though low, would not prevent these oscillators from being used industrially were it not for the fact that they cannot be scaled up Very large quartz crystals do not exist and mechanical considerations also would certainly limit their size Hence, to irradiate bulk quantities of materials a large number of units is necessary and construction cost would be very high in relation to the volume treated

The second disadvantage of a piezoelectric crystal oscillator is that it is very difficult to irradiate aqueous solutions directly because the two faces of the crystal are at very high voltages They must therefore be surrounded by an insulating liquid such as transformer oil, for even in air there is a tendency for sparking to occur across the two faces resulting in immediate damage to the crystal To transmit the sound from oil to water through say a glass vessel is most inefficient because up to 80 per cent of the energy would be lost in the glass It is possible, however, to have one face of the crystal in contact with water and the other in oil, the apparatus shown in *Figure 1* having been used successfully by the author, but there is always a danger of water leaking through the rubber flange

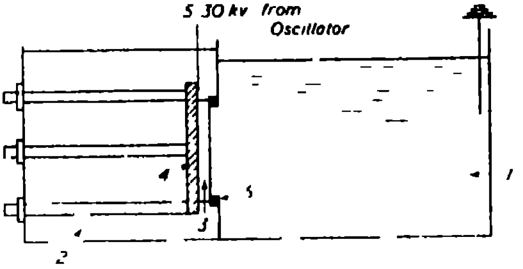

Figure 1 Apparatus for irradiating water directly with a quartz crystal 1 Perspex box filled with water, 2 compartment filled with transformer oil, 3 quartz crystal 4 metal plate held tightly to back of crystal by bars 5 rubber flange

A piezoelectric generator, although most valuable for research, holds out little prospect for large scale application

Magnetostriction generator—Some ferromagnetic materials, notably nickel, contract when placed in a magnetic field and this property can be utilized for the production of sonics and ultrasonics Usually a nickel tube or rod is suspended half way along its length and placed inside a solenoid which is coupled to an oscillator The length of the tube must be such that its natural elastic frequency is the same as that of the magnetic field produced in the solenoid

Instead of tubes, experiments with nickel laminates were made in Germany during the 1939–45 war[2] The best constructional details are found in N GAINES and L CHAMBERS' paper[3] even though it was one of the earliest to be published Unfortunately, there is no such excellent description as is available for piezoelectric oscillators The literature describing the best coupling between the high frequency electric generator and the mechanical system is unsatisfactory In the author's laboratory it was found necessary to spend considerable time in determining the best method of coupling a magnetostriction generator and there is a need for an authoritative treatment of this problem from the electrical engineering side The efficiency of an oscillator of this type is probably only 20 per cent, although very much higher figures (50–70 per cent) are claimed for the German nickel laminates The inevitable losses due to eddy current heating in the nickel and heat losses in the solenoid make this latter claim suspect in the author's view and about 30 per cent probably represents the upper limit of efficiency The frequency band for high intensity work is 5–50 kc/s although it is alleged that the laminates can be worked as high as 200 kc/s It is obviously most important that studies should be made and published in this country concerning the performance of flat nickel laminates, to check the German Admiralty research claims which, if corroborated, would open up important possibilities for the application of ultrasonics

Magnetostriction oscillators, like quartz oscillators, cannot be scaled up for industrial use as their dimensions are governed by the mechanical properties of the magnetostrictive material Large quantities of materials can thus only be treated by having a multiplicity of units However, the metal tube carries no current and can thus radiate directly into water, in this way overcoming one of the most serious difficulties of the crystal oscillators

The author has noticed that the life of a nickel tube is short as it appears to fatigue after a few hours running, with a resultant great loss in sound intensity This difficulty can be overcome to some extent by using alloys, although research will have to be carried out to determine optimum compositions

Electromagnetic generator— H W St Clair[4], at the U S Bureau of Mines, has designed a powerful generator for sonics and ultrasonics on the basis of a loudspeaker employing a hollow aluminium tube as diaphragm Full constructional details are given for oscillators up to 20 kc/s which would appear to be near the upper limit for high intensities An efficiency of 30 per cent has been obtained, eddy current heating again being the greatest cause of energy losses Although St Clair only irradiated gases there should be no difficulty in working in water or any other liquid Compared with a magnetostriction generator, the oscillating system is mechanically intricate On the whole, however, these two magnetic methods appear very similar, both in their potentialities and limitations In the absence of published data it is impossible to decide which is more efficient A thorough study of the various factors influencing the efficiency of conversion of electricity to sound for the different generators is required It should be possible to estimate unavoidable losses, for example, those occurring in the coupling of the mechanical vibrator to the high frequency circuit, and to give the theoretical overall efficiency However, at the moment, no estimate can be given of this figure for the different generators nor are there any reliable data for the actual efficiencies of the various methods

Mechanical generators— Several mechanical generators for the production of ultrasonics in air have been known for a long time and studied in considerable detail The best known of these is the Galton generator which functions on the usual whistle principle of a vibrating gas space, but is incapable of producing very high energies The Hartmann generator[5], on the other hand, is capable of vibrating in air at 20 kc/s with as much as 20 watts and with lower energies at much higher frequencies The Hartmann oscillator also makes use of a resonating air space, but is energized by an air or gas stream moving at supersonic velocity (air issuing from a jet with an excess pressure of 0 9 atm moves at supersonic velocity) In this way zones of instability are produced which give intense acoustic vibrations if the opening of the resonator space is made to coincide with the point of instability in the gas stream

From a practical point of view the generation of ultrasonics in liquids or solids is of much greater value than their production in gases, and the development of a suitable purely mechanical oscillator would represent a great advance The obvious suggestion is to actuate a whistle immersed in a liquid with a liquid The principle of the Galton whistle cannot, however, be used as it requires complete reflection, as is found with gases, between the vibrating volume and the wall of the resonator However, this does not apply if a liquid is used, since there is no great difference in velocity of sound between liquids and solids, unlike gas/solid systems As a result, if a Galton whistle is operated under a liquid the sound waves penetrate the wall and no reflection and accompanying resonance reinforcement takes place There are no solids known to the author which can reflect sound waves in a liquid without serious loss

In addition, the Hartmann generator cannot be used with liquids since it would require a column of liquid moving at supersonic speed Such velocities cannot be realized with liquids without great difficulty, if at all, and would certainly not be controlled without the most elaborate installation The enormously greater kinetic energy of a supersonic jet of liquid as compared with one of gas arises from the fact that the velocity of sound in water is five times that in air and the ratio of the densities is approximately 1 1,000

To design a ' liquid ' whistle, therefore, a new principle had to be found which did not involve reflection of a sound wave from a solid interphase This appears to have been done by R Pohlmann of Siemen and Schuckert Unfortunately, no publications describing such a machine and its performance are available and the only information comes from the author's *B I O S Report* on ultrasonic research in Germany[6]

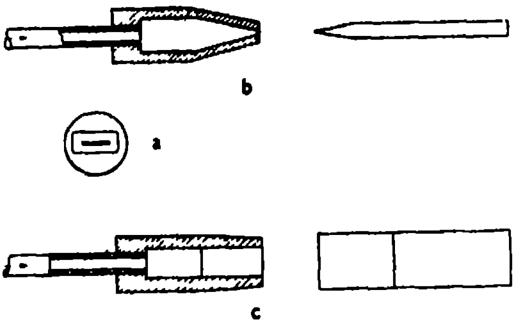

Figure 2 Pohlmann whistle a *cross section of nozzle,* b *cross section of whole whistle,* c *plan of whole whistle*

The best of these methods, *Figure 2*, consists of a jet of liquid impinging against a steel blade When the jet hits the blade the latter vibrates at its natural frequency and transmits the oscillations to the surrounding liquid The frequency of the sound waves produced depends naturally on the mechanical properties of the blade Pohlmann claims to have operated at frequencies from 3–33 kc/s, but was unable to give any detail of operation or of the efficiency of conversion of the kinetic energy of the jet to sound energy In this laboratory we have built a number of such whistles to study their uses in emulsification and other problems, *vide infra* The water was expelled with a gear pump and the orifice size was adjusted so as to give a jet at about 10–20 atm pressure For the vibrator, an *Ever-Ready* razor blade was found best and this was clamped about 1 cm from its edge thus giving a frequency of about 15 kc/s Such a whistle was very effective for the emulsification of two liquids, one being blown through the orifice into the other and the resulting emulsion recycled through the whistle, *Figure 3*, to ensure thorough emulsification

The inlet to the gear pump was placed at the liquid surface if a liquid lighter than water was emulsified and at the bottom of the vessel if a liquid heavier than water was used Thus, should the emulsion break, the liquid was recycled immediately

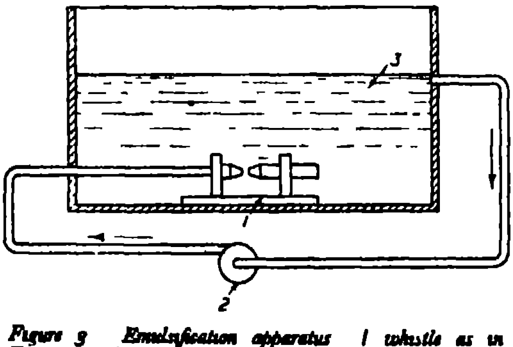

Figure 3 Emulsification apparatus 1 whistle as in Figure 2, 2 gear pump, 3 vessel containing emulsion

The intensity of the sound waves was greater than that due to the oscillations of the small blade An additional effect which appears to be more important than the vibrations transmitted from the blade is that of the deflection of the jet As the blade set directly opposite the narrow jet vibrates the latter is deflected up and down and sets up very powerful vibrations in the liquid of its own account

There is need for much research into this whistle, for example, it is necessary to relate the jet pressure with the amplitude of the vibrations, to find the frequency limits, to determine the optimum working conditions and the efficiency There is, no doubt, also scope for redesigning the simple jet and blade system to give a still more effective whistle

The great cost of electrical generators requiring as they do large high frequency oscillators has up to now effectively prevented their use in industry other than as a research tool This applies particularly to piezoelectric generators where the high voltages involved create great additional problems The Pohlmann whistle, however, holds out real promise for large scale application and in the author's view makes possible for the first time the application of ultrasonics to such processes as emulsification Recent work with magnetostriction generators appears also to make possible their industrial use, but for simplicity of construction and robustness they cannot compete with the whistle

Before intense ultrasonics can be used in industry the effect on the operator of prolonged exposure to them will have to be determined

CHEMICAL AND PHYSICOCHEMICAL EFFECTS

All the many diverse phenomena such as emulsification of liquids, dispersion of solids, precipitation of smokes, decreasing grain size during crystallization, degassing of liquids, breaking up macromolecules, activation of dissolved oxygen leading to powerful oxidation, prevention of metal passivity, increasing rate of dyeing and chemical reactions, sterilization and medical effects produced by powerful mechanical vibrations, can be ascribed either to cavitation or to the enormous accelerations of particles in the sound field

When irradiating a liquid with ultrasonics, heat is invariably produced and it is important to ensure that the effects ascribed to the ultrasonics are not really caused by the heat alone.

An ultrasonic wave produces very violent dispersions of two media into one another because of the very great acceleration of the particles and molecules in the beam which may be as much as $500\ \text{km/sec}^2$. At high intensities the liquid is ruptured and cavitation occurs

EFFECTS PRODUCED BY CAVITATION

W A WEYL and E C MARBOE[7] in a recent article in this journal have discussed the cavitation of water with ultrasonics They consider a volume of water as one large molecule which, on rupturing by cavitation, leaves free valencies similar to those produced when a sheet of mica is split This theory satisfactorily accounts for the oxidation of metal ions, dyes, halide ions, the production of hydrogen peroxide and luminescence and a host of miscellaneous oxidation effects observed on irradiation of aqueous solutions None of these effects occurs when the intensity is not great enough to produce cavitation or when this is prevented by compressing the solution[6] The oxidizing effect of ultrasonics in aqueous solutions is enhanced by the presence of small quantities of a second phase of a non-polar substance such as carbon tetrachloride[6], presumably because cavitation of water occurs more readily at a non-polar interface

With ultrasonic irradiation, almost any liquid can be emulsified with any other *e g* it is the only method of emulsifying mercury in water, and most solids can be colloidally dispersed in water This phenomenon has been studied in detail by K SOLLNER[10] and M FREUNDLICH[11] who have shown that acoustic waves also coagulate and that an equilibrium is reached when emulsifying two liquids , thus, 4 per cent is the limiting concentration which can be attained for toluene in water and emulsions of higher concentrations will be coagulated Cavitation at the interface of the two liquids is responsible for the emulsification with the exception of mercury sols which behave anomalously Coagulation is due to the increased rate of movement of the individual particles which will tend to accumulate wherever stationary waves occur *i e* orthokinetic coagulation The precipitation of smoke is caused in a similar manner and the particles accumulate always at the nodes, or antinodes Hence, emulsification occurs entirely at the interphase whereas coagulation proceeds in the interior of the aqueous phase

The use of ultrasonics for polymerization of emulsions of vinyl monomers was found by the author[12] to give a superior product because it is not necessary to have an emulsifying agent present which often spoils the electrical and mechanical properties of the resulting polymer Using the Pohlmann whistle, moreover, the emulsions can be prepared simply and continually recirculated to prevent their breaking, *Figure 3*

Cavitation, however produced, invariably results in powerful degassing of the solution and this is undoubtedly the explanation for the remarkable degassing effects of ultrasonics Water and simple solvents can be easily de-aerated and the method has even been applied to the degassing of metallic melts so as to obtain improved casting It is impossible to de-aerate transformer oil as the ultrasonics depolymerize the hydrocarbon, and volatile breakdown products such as hydrogen and benzene are evolved in increasing quantities after the air has been removed

Cavitation at the interphase probably also accounts for the removal of oxide films from metals immersed in water and other liquids Water does not tear away easily from hydrophilic surfaces such as oxides and hence cavitation occurs at the interphase of metal and oxide films resulting in the breaking off of the latter Aluminium can be soldered after being irradiated in flux because the protective oxide film has been split off A similar explanation no doubt holds for the breakdown of fibrous specimens into fragments small enough for electron microscopy In the same way, bacteria are torn apart in an ultrasonic beam whose sterilizing action can no doubt be explained partly by the production of active oxygen coupled with the mechanical disruption of the organism Colloidal matter added to a suspension of bacteria largely prevents the sterilizing action of ultrasonics , for example, bacteria killed in a few seconds in a saline suspension survive for hours in irradiated milk[6]

When metallic melts are irradiated during cooling, crystallites produced in the solid are very much smaller than in the absence of ultrasonics but whether cavitation is essential for this effect is not known[13] For example, with zinc, ultrasonics produced a grain size one tenth the normal The rate of crystallization from supersaturated solutions is greatly increased by irradiation with ultrasonics Professor H HERTZ succeeded in speeding up the refining of sugar in this way and large scale application of the process in Germany was said to have been prevented only by the war[6] In all probability the effect is due to cavitation which, occurring at crystal nuclei, will break these up and increase the supply of centres for crystal growth , possibly a similar explanation accounts for the finer grain sizes obtained with ultrasonics

EFFECTS NOT DIRECTLY CAUSED BY CAVITATION

Ultrasonics are very effective in depolymerizing large molecules in solution and the reactions with polystyrene, nitrocellulose[14], starch and proteins[15,16] have been studied in detail There seems little doubt that sufficient energy to rupture chemical bonds can be derived from the very great frictional forces set up by the relative motions of solvent and macromolecule in an intense ultrasonic field J SCHMID[18] showed that the depolymerizing effect with polymethylmethacrylate was independent of the frequency used The denaturation of proteins in aqueous solution by ultrasonics is probably not caused by the actual rupture of the molecules but by an unfolding of the globular shape under the great shearing forces The liquefaction of gels undoubtedly has a similar explanation

Wool can be made unshrinkable by exposure to ultrasonics[19] Undoubtedly the scale structure on the surface of the fibre is disrupted but without further research it is impossible to say whether this is attributable to the active oxygen produced, to mechanical disruption at the interphase *i e* like removal of oxide film from metal, or to denaturation as for a soluble protein

Ultrasonic irradiation of metals usually decreases their anodic polarization and markedly reduces chemical passivity[20] The mechanical removal of a surface oxide film does not offer a complete explanation for the observations and thus is obviously a topic which is well worth further investigation

Many claims have been made that ultrasonics speed up or modify the course of a homogeneous chemical reaction Generally, insufficient precautions were taken to remove the heat produced and the rise in temperature would probably be sufficient to account for the results There are, however, a few reactions which are undoubtedly accelerated *e g* the hydrolysis of potassium persulphate[21] and the decomposition of benzazide[22] It is possible that the active oxygen produced functions as a catalyst or that the reactions are in fact heterogeneous and that cavitation at the wall is responsible for the increased rate

Many heterogeneous reactions, such as the dissolution of metals in acid or their attack by sulphide ions[23], are greatly speeded up by irradiation with ultrasonics The explanation which seems most probable is that there is a reduction of the resistance of the so-called Nernst diffusion layer of liquid next to the solid which is present even under the most efficient stirring conditions and is frequently rate controlling in heterogeneous reactions This hypothesis is supported by the observation that diffusion through membranes is greatly accelerated by ultrasonics[24]

Russian workers have shown that ultrasonics accelerate the dyeing of cotton[25] and the same effect was observed in this laboratory for the dyeing of wool The rate of all dyeing processes is diffusion controlled and there seems no doubt that ultrasonics again disturb the diffusion layer of liquid next to the fibre, probably because of cavitation In all probability, ultrasonics also effect dyeing by breaking up aggregated dyes into smaller, if not molecular, units but no data are available on this point

Dr R POHLMANN[4] has studied the therapeutic effects of ultrasonics by using these to give 'depth massage' to patients suffering from rheumatic diseases Spectacular cures for sciatica and neuralgia are claimed It would appear vital that these investigations should be repeated in this country for if confirmed a new and important therapeutic tool would be at hand

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Rapid Analysis of Silicates

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As an example of the rapid analysis of silicates we will take the analysis of clays These naturally occurring products have very variable compositions, but it is possible to fix the limits of the different constituents between the following values, *Table I*

Table I

Range of Constituents in Clays

Constituent	*Per cent range*
SiO_2	38 –94
Al_2O_3	2 –52
Fe_2O_3	0 1 –18
TiO_2	0 1 – 3
CaO	0 01– 3
MgO	0 01– 3
K_2O	0 05– 5
Na_2O	0 03– 3

METHODS OF ANALYSIS OF CLAYS

Every analytical chemist knows the theory or practical procedure of the classical methods for the separation of these constituents

1 fusion with sodium carbonate, precipitation and purification of silica ,

2 determination of the oxides Al_2O_3, Fe_2O_3, and TiO_2 ,

3 precipitation of calcium oxalate and ignition to calcium oxide ,

4 precipitation of magnesium ammonium phosphate and ignition to magnesium pyrophosphate ,

5 the method of L SMITH for the determination of sodium and potassium oxides

It is well known that such an analysis is very time consuming, that the best accuracy obtainable is of the order of 1 per cent, and that the total of the elements determined as oxides is frequently equal to 101 per cent or even more In addition, an investigation carried out in the United States of America in 1906 showed that the analysis of the same sample of argillaceous rock, conducted in several laboratories specializing in silicate analysis, led to very discordant results, even for the analysis of the fundamental elements

The important part played by specialized chemists such as W F HILLEBRAND and G E F LUNDELL[1] in establishing recommended analytical procedures as standard methods for mineral analysis is widely recognized In spite of this, these standard classical methods remain long and difficult, and require the training of qualified analysts Thus it is highly desirable to have available analytical methods for clays which can rival the classical methods in accuracy whilst allowing results to be obtained in far less time and by the use of less highly trained analysts

The spectrochemical methods of analysis have been put to use in this field, partly through absorption spectroscopy (or colorimetry) and partly through emission spectrography by means of an arc or spark The colorimetric method has been perfected by R HEDIN[2] of the Royal Institute of Technology of Stockholm , the emission spectrography method has been perfected by J GILLIS and J EECKHOUT[3] of the Analytical Chemistry Department of Ghent University

We shall here briefly compare these two methods which both show advantages for the analysis of clays and natural and artificial silicates *e g* cements and blast furnace slags

COLORIMETRIC METHOD

Hedin prepares three solutions of the clay sample The first solution, for determination of SiO_2, Al_2O_3, Fe_2O_3, and TiO_2, is obtained by fusion of 0 2 gm clay with sodium carbonate, precipitation of gelatinous silica by hydrochloric acid, filtration from chlorides of iron, aluminium, and titanium, and solution of the silica in sodium hydroxide to form sodium silicate Each filtrate is made up to 1 litre. The silica is determined colorimetrically in this solution by the yellow colour produced on forming silicomolybdic acid, the Al_2O_3 by the yellow colour formed with aluminon, the Fe_2O_3 by the red colour formed on addition of potassium thiocyanate, and the TiO_2 by the yellow colour produced by hydrogen peroxide

The second solution, for the determination of calcium and magnesium oxides, is obtained by fusion of 0 5 gm clay with sodium carbonate, precipitation of silica with hydrochloric acid, addition of hydrogen peroxide to dissolve MnO_2 as the chloride, precipitation of iron, aluminium, and titanium as their hydroxides by ammonia, and filtration of the solution into a 250 ml graduated flask The precipitate is re-dissolved in hydrochloric acid, re-precipitated by ammonia and washed with four portions of 2 per cent ammonium chloride solution The washings are added to the filtrate in the 250 ml flask, the whole acidified with hydrochloric acid, and made up to 250 ml Calcium oxide is determined by precipitation as calcium oxalate and titration with decinormal potassium permanganate in the presence of dilute sulphuric acid Magnesium oxide is determined colorimetrically by means of titanium yellow which, on co-precipitation with magnesium hydroxide, produces a red coloration

The third solution, for determination of alkalis, is obtained by treating 2 gm clay with hydrofluoric and sulphuric acids, followed by neutralization with ammonia to *p*H 5 (methyl red) and washing of the precipitate with hot water The filtrate is made up to 200 ml in a graduated flask Sodium oxide is found by precipitation with zinc uranyl acetate and estimated colorimetrically by the brown coloration formed with uranium in presence of hydrogen peroxide and ammonium carbonate Potassium oxide is found by precipitation with chloroplatinic acid and addition of potassium iodide, when a red coloration is formed due to the PtI_6^{2-} ion

Hedin gives a similar scheme of operations and shows that the complete analysis of a clay can be finished within eight hours

As for the analysis of kaolin, for example, these results are comparable in every way, according to Hedin, with the results obtained by classical gravimetric methods, see *Table II*

Table II Analysis of Kaolin

Constituent	*Gravimetric analysis per cent*	*Colorimetric analysis per cent*
SiO_2	46 6	46 6
Al_2O_3	37 6	37 8
Fe_2O_3	0 8	0 7
TiO_2	0 1	0 1
CaO	0 1	0 1
MgO	0 2	0 1
K_2O	1 8	1 7
Na_2O	0 3	0 3

Hedin's method is equally applicable to the analysis of mica, feldspar, sands, slags from blast furnaces, and cement It requires a combined colorimeter and nephelometer with two photoelectric cells of the selenium barrier layer type, connected by a compensating circuit to a galvanometer as null point indicator Its use is very simple and calibration is carried out with standard solutions of known composition This method constitutes an appreciable advance in the analysis of silicates, especially in industrial analysis

EMISSION SPECTROGRAPHIC METHOD

The method of analysis based on emission spectrography involves the preparation of a 'master solution' for the determination of Al_2O_3, Fe_2O_3, TiO_2, CaO, and MgO This is made up by dissolving 1 gm clay in hydrofluoric and sulphuric acids in a platinum crucible so as to volatilize the silica After evaporation to dryness the residue is taken up in hydrochloric acid and warmed to dissolve the salts completely This is again evaporated to dryness and re-dissolved in 10 ml of a standard copper sulphate solution containing 2 5 gm copper in 1 litre of 2N HCl A measured quantity (0 02 ml) is evaporated on a graphite electrode of 5 mm diameter with a flat surface, previously cleaned by a preliminary discharge for 60 seconds The upper electrode is also of graphite and the excitation is by intermittent arc (2 periods of arc discharge for 10 periods of extinction) The intensity of the lines is compared with that of the copper, which furnishes an internal standard The curves produced permit of the determination of the following

Al_2O_3 at a concentration range of 50–1 per cent
Fe_2O_3 at a concentration range of 20–0 1 per cent
TiO_2 at a concentration range of 3–0 1 per cent
CaO at a concentration range of 3–0 1 per cent
MgO at a concentration range of 3–0 01 per cent
Na_2O at a concentration range of 5–1 per cent

For the determination of sodium oxide down to concentrations of about 0 1 per cent and of potassium oxide down to about 0 4 per cent, the master solution described above must have 1 ml of a lithium carbonate solution containing 10 per cent lithium added to it as an internal standard For the determination of still lower concentrations of sodium and potassium oxides, recourse must be made to chemical concentration of a solution of the sulphates In order to do this, 1 gm of the clay is treated with hydrofluoric and sulphuric acids, evaporated to dryness, and ignited at 900°C This ignition decomposes the sulphates of the tetravalent metals (Ti), trivalent metals (Fe and Al), and magnesium, to insoluble oxides On taking up the residue again in water, nothing remains in solution except sodium and potassium sulphates and very small amounts of calcium and magnesium sulphates The aqueous solution obtained by extraction of the ignited sulphates is evaporated to dryness and the residue dissolved in 1 ml of the same solution of copper as was used for the master solution

A drop (0 02 ml) of this solution, evaporated at 90°C on a 5 mm diameter Hilger graphite electrode, after absorption and evaporation of a drop of xylene, deposits a small crust of salts in position With an intermittent arc one may carry out determinations of sodium down to 0 02 per cent and potassium down to 0 2 per cent (as the oxides) With an infrared sensitive plate it is possible under the same conditions to go down to 0 005 per cent for sodium oxide and 0 02 per cent for potassium oxide The mean error of all these results is of the order of 6 per cent of the figure obtained

Silica is determined by difference, after the addition of the various percentages found This is the weak point of the technique based on solution in a hydrofluoric/sulphuric acid medium otherwise the method is perfectly reproducible and extremely rapid, a single solution is sufficient in practice provided that the alkali metals do not have to be determined at low concentrations

Still more rapid determinations may be carried out by working directly on a specimen of finely powdered clay In order to do this, 0 1 gm clay, 0 4 gm copper oxide, and 0 5 ml alcohol are mixed in an agate mortar and ground finely until the alcohol has completely evaporated The mixture is dispersed in 1 ml alcohol, and, in order to deal with the whole of the suspension, it is withdrawn by means of a glass tube of diameter less than that of the flat electrode, and placed on the electrode, the alcohol disappears by absorption and evaporation

With sparking, the powder on the electrode is not projected, and under these conditions the excitation can be carried out in a very reproducible way The standardization curve must always be established using natural clays, analysed by classical gravimetric methods The physical nature of the argillaceous mineral is very important here

Thus one may determine the following down to the minimum concentration indicated

SiO_2 in all proportions
Al_2O_3 in all proportions
Fe_2O_3 down to 1 per cent
TiO_2 down to 0 5 per cent
CaO down to 0 5 per cent
MgO down to 0 3 per cent

Sodium and potassium oxides cannot be determined in this way, since the spark method is too insensitive The reproducibility for the other elements of this method on powder is excellent, with a mean error of 3 to 5 per cent The analysis of a powdered clay is extremely rapid, it consists of the time required for mixing with copper oxide and grinding in alcohol, taking one negative, developing and drying, measuring a dozen wavelengths photometrically and reading the percentage composition from the calibration diagrams In total a maximum of fifteen to twenty minutes is required for the determination of the principal constituents, except for the alkali metals For the latter it can be stated that the preparation of a solution and the determination can be carried out in comparable times by the emission and colorimetric methods

Blast furnace slags[4] have the mean composition shown in *Table III*

Table III

Range of Constituents in Blast Furnace Slags

Constituent	*Per cent range*
SiO_2	3 -30
CaO	45 -60
MgO	1 -20
FeO	3 -30
MnO	2 -20
Al_2O_3	1 - 5
P_2O_5	0 1- 3

They can be analysed by a spectrographic method analogous to the above on powder, using either 30 mg with 90 mg copper oxide (as diluent and internal standard) or 30 mg with 90 mg graphite (as diluent), in each case using Fuessner's condensed spark technique

The mean square errors for a single determination are 6 per cent for Mg, Mn, and Al, 7 per cent for Fe, and 9 per cent for Ca On the other hand the results are obtained in less than 15 minutes with sufficient precision for industrial analytical control of blast furnace slags

The same method is applicable in principle to the analysis of mica, feldspar, cement, and in general silicates of fixed type, after preliminary construction of calibration curves

Spectrographic analysis, by emission, of powdered substances (clays or blast furnace slags) necessitates standardization, not with artificial mixtures of oxides, but with natural silicates of the same type, previously analysed by classical gravimetric methods We cannot emphasize this point enough it is essential for obtaining satisfactory results by our method If these types of natural silicates are not available, methods using solutions must be relied upon Artificial mixtures of oxides can then be employed by treatment with hydrofluoric and sulphuric acids and combination with the copper sulphate solution described above

Thanks are due to J Bowler Reed for translating this article

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Permanent Magnet Association

Central Research Laboratory

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It is well known that the strength of permanent magnets has greatly improved during the last few years[1], an improvement due mainly to the increase in coercive force of permanent magnet materials Hence it can be understood that modern permanent magnets have properties which could not be satisfactorily explained by any theory until comparatively recently

It was with a view to this lack of fundamental knowledge that the Permanent Magnet Association decided, in 1942, to set up the Central Research Laboratory The work of this unit is divided into a number of sections, the most important of which is the further development of practical materials aiming mainly at the improvement of energy content *i e* efficiency of permanent magnets of a given volume However a substantial effort is also devoted to the study of those physical properties of alloys which are thought to be of basic influence on magnetic properties, especially on coercive force The study of fundamental problems is of great assistance to the practical technologist who is aiming at a better commercial product

In order to appreciate the problems which are met with in the fundamental study of magnetically hard substances it is necessary to give a brief outline of our present state of knowledge of those features which influence magnetic properties, especially coercive force

For the design of an efficient permanent magnet the most important characteristic of the material must be a high $(BH)_{max}$ A permanent magnet in ordinary circumstances works under the influence of its own demagnetizing field, hence the working point will lie somewhere on the demagnetization curve, *Figure 1* The $(BH)_{max}$ point is that point on the curve at which the product of induction B and field strength H is a maximum, this product is proportional to the maximum value of energy which a given volume of magnet material can deliver into an air gap[2] It is not difficult to understand that for this product to be high both remanence and coercive force should be high, furthermore the demagnetization curve should be as full as possible *i e* it should approximate as far as possible to a rectangle Early materials used for permanent magnets, such as carbon and tungsten steel[1], had remanence values of the order of 10,000 gauss and, having regard to the highest values of intrinsic magnetization of any known material, a great improvement in remanence cannot be expected The early materials had coercive forces of about fifty oersted, and there the greatest improvements have taken place The best modern permanent magnet alloys have coercive forces of the order of 1,000 oersted

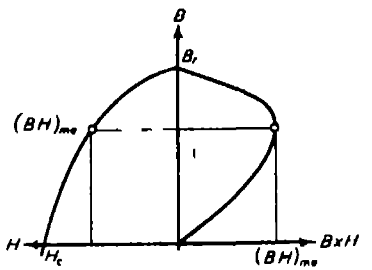

Figure 1 Demagnetization curve and energy product curve for a permanent magnet material

PHYSICAL AND METALLURGICAL CONSIDERATIONS IN PERMANENT MAGNET MATERIALS

Among the physical and metallurgical conditions which have to be fulfilled in order to obtain high coercive force the most important is the development of a high degree of heterogeneity in the material In order to illustrate this in more detail let us remember that any magnetic material is divided into a large number of domains each of which is spontaneously magnetized to saturation Any change in the overall magnetization can only be brought about either by movements of the boundaries between the domains or by rotations of the magnetization vectors within the individual domains

It has been shown that at each point in any magnetic material the magnetization will lie in that direction which is a so-called easy direction *i e* a direction in which it requires least energy to magnetize the material *Figure 2* shows the energy distribution for a point in a cubic lattice, in curve a the energy distribution arising from magnetocrystalline anisotropic forces alone is given R BECKER[3] and colleagues have shown that the energy distribution curve can be modified if stresses are present in the material, and the easy direction of magnetization need not necessarily coincide with a principal crystallographic axis, *Figure 2* curve b In order to produce a rotation of the magnetic vector from one stable position to another an energy maximum must be overcome, in ordinary materials such as soft iron

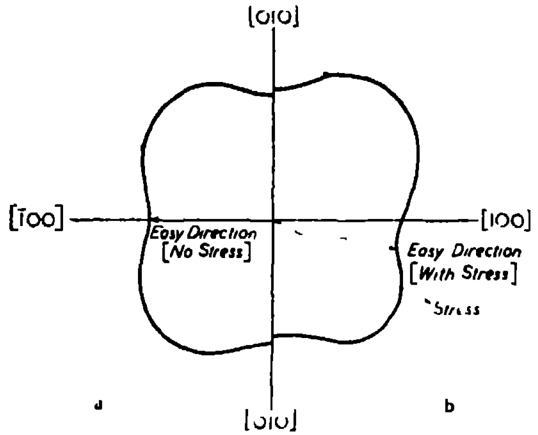

Figure 2 Distribution of energy of magnetization in cubic material a stress free material b material under stress

movements of domain boundaries usually take place long before the magnetizing force necessary for such a rotation is reached For example if no boundary movements took place the coercive force of pure iron would be about 100 oersted, while actual measured values are only of the order of 1 oersted This is indirect evidence that boundary movements take place before irreversible rotations If we now consider that boundary movements occur before such rotations from one stable position into another, one problem of interpreting coercive force is the estimation of fields necessary for irreversible boundary movements The coercive force corresponds to the average value of field required for irreversible changes, either boundary movements or rotations, to take place

The boundary between two domains is a layer of some hundred atoms thick in which the vector of magnetization changes its direction gradually from that of one domain to that prevailing in the other Such a boundary possesses an energy equivalent to a surface tension which depends on the exchange interaction between neighbouring atoms, the magnetocrystalline energy and any irregular stresses or lattice imperfections The first two contributing factors are constant throughout a crystal but the third varies from place to place and influences the boundary energy in a rather complicated way However the boundary tends to take up a position in which its total energy is a minimum, such a position is stable On the application of a field the boundary will be moved as indicated in *Figure 3*, if it is moved far enough to overcome a local maximum it can glide into another stable position, thus having undergone an irreversible displacement

If the microstresses and lattice irregularities are accurately known the field required to produce such displacements can be calculated In the absence of such exact knowledge, however, simple models have to be devised A model which has been used extensively for materials containing large microstresses has been proposed by Becker[3] and the coercive force can be calculated accordingly as

$$H_c = p_1 \frac{\lambda_s z_i}{J_s} \tag{1}$$

where p_1 is a function of the parameter δ/l, δ being the boundary thickness, and l the average wavelength of energy variation, z_i is the average value of the microstresses, λ_s the saturation magnetostriction constant and H_c and J_s have the conventional significance of coercive force and saturation magnetization respectively The factor p_1 takes a maximum value of $\frac{2}{3}$ in a material in which the stress variations have a wavelength of about half the boundary thickness

In materials where the crystal anisotropy is large, variations in microstresses will not influence the domain boundary energy significantly In pure iron, for instance, stresses associated with an energy equivalent to the magnetocrystalline anisotropic energy are considerably beyond the tensile limit and it is difficult to see how such stresses could be present This fact was recognized some years ago, consequently an alternative model was suggested by M KERSTEN[4] in which obstacles to boundary movements were attributed to non-magnetic inclusions Since the boundary energy is constant throughout a crystal in which the stress contribution is small compared with that arising from the magnetocrystalline energy, the total boundary energy depends only on the total boundary area, consequently if a boundary includes a non-magnetic particle its extent will be reduced and such a position will be a stable boundary position In *Figure 4* a model is shown in which a boundary would have stable positions in those places where a majority of non-magnetic inclusions are part of the boundary Upon application of a magnetic field the boundary will tend to move

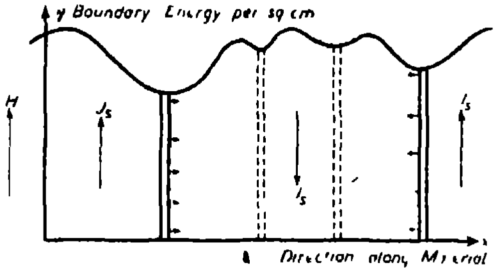

Figure 3 Irreversible movement of 180° domain boundary

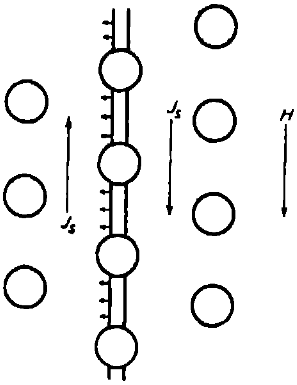

Figure 4 Domain boundary in stable position due to non-magnetic inclusions Field H tends to move boundary in direction of small arrows

and at a certain field an irreversible jump into the next stable position will occur The average field required to cause such a jump can be calculated, giving a coercive force of

$$H_c = 2.5\, p_s \frac{K}{J_s}\, v^{\frac{2}{3}} \qquad (2)$$

where v is the total fractional volume of non-magnetic inclusions, K is the constant of magnetocrystalline energy and p_s a function of δ/d, δ being the boundary thickness and d the average diameter of the inclusions Maximum coercive force is achieved when the diameter of the inclusions is equal to the boundary thickness, p_s then becoming $\frac{1}{4}$ A serious criticism of Kersten's inclusion theory is that it neglects the contribution of the self-demagnetizing energy associated with the non-magnetic inclusions, which depends entirely on the shape and size of the inclusions For spherical inclusions of diameter equal to the domain boundary thickness in iron the energy term arising from this cause would have about a hundred times the value of the domain boundary energy change between stable and unstable positions It is clear that consideration of this demagnetizing energy is complicated and would alter the calculated coercive force decisively For laminar inclusions or for large non-magnetic inclusions some of the ideas of Kersten's theory remain applicable

The expressions for coercive force arrived at by both theories which attribute magnetic hardness to obstacles in the movements of domain boundaries rely on the assumption of periodic and regular stresses or inclusion patterns as well as on plane domain boundaries There is evidence that in many substances these assumptions would be fulfilled, but such assumptions are not satisfactory for the general theory In fact if the various physical properties of some permanent magnet materials are measured the correspondence with either of the above theories is somewhat unsatisfactory The theoretical conditions have been examined in detail by L Néel[3], who found that if no assumptions about regularity of domain boundary and lattice faults are made, calculated coercive forces are only a *few* per cent of the measured values Néel has therefore proposed a different mechanism responsible for stable domain boundary positions If a material is perturbed by inhomogeneity or stresses the spontaneous magnetization within a given region is not quite uniform and we have the equivalent of small islands of free magnetic charges Such islands represent a high internal energy and if they are bisected by a boundary forming magnetic dipoles with a smaller moment the total energy of the assembly is reduced This is illustrated by *Figure 5* where under a an unstable and under b a stable domain boundary is shown The thickness or energy content of the domain boundary becomes of secondary importance and obstacles to boundary movements are entirely dependent on the perturbation of the magnetization intensity itself which can be due to irregular stresses or heterogeneous inclusions The mathematical evaluation of the coercive force based on this model is very difficult, but Néel has carried out the calculation, arriving at the following expressions With the perturbation due mainly to irregular stresses the coercive force becomes

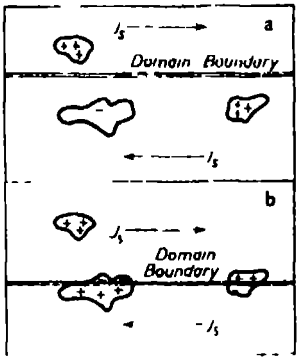

Figure 5 a unstable b stable positions of domain boundary in a medium perturbed by islands of free magnetic charges

$$H_c = \frac{4}{\pi}\,\frac{v'L}{J_s}\,\frac{(\frac{3}{2}\lambda_s\sigma_i)^2}{K + \frac{3}{2}r\lambda_s\sigma_i}\left\{1.386 + \log_e\left(\frac{2\pi J_s^2}{K + \frac{3}{2}r\lambda_s\sigma_i}\right)^{\frac{1}{2}}\right\} \qquad (3)$$

where all symbols have the same significance as before and L and r are parameters depending on the ratio of magnetocrystalline energy to stress energy v' represents the fraction of the total volume which is subject to perturbations or irregularities

If the perturbations are due to heterogeneity *i e* to an irregular variation of the absolute value of the spontaneous magnetization, we arrive at the coercive force

$$H_c = \frac{2}{\pi}\frac{K}{J_m}\,\frac{\overline{J_s^2} - J_m^2}{J_m^2}\left\{0.386 + \log_e\left(\frac{2\pi J_m^2}{K}\right)^{\frac{1}{2}}\right\} \qquad (4)$$

where $\overline{J_s^2}$ is the mean square of magnetization and J_m the arithmetic mean of the saturation magnetization *i e* the value measured in a macroscopic sample

Equation 4 has been found to be of interest in the study of permanent magnet alloys and it has been possible to measure most of the quantities appearing in this formula Before discussing our own experiments it is of importance to mention the significant contribution made to the theory by E C STONER and E P WOHLFARTH[6]

Let us consider a small element in the shape of a cube of magnetic material The element can either be magnetized uniformly *i e* it can be a single domain , in that instance there is associated with this arrangement a demagnetization energy $\frac{1}{2}NJ_s^2$ where N is the demagnetizing coefficient Alternatively the element can consist of several domains so that the surface magnetization disappears as in an ordinary non-magnetized body There is then an energy associated with the domain boundaries which can be shown to be of the order

$$F_l = I \sin^2 \left(\frac{\pi a}{2l}\right) \quad 2 \frac{l^2}{a^2} \tag{5}$$

where I is the exchange saturation energy per atom, a the lattice parameter, and l the length of cube edge

It is clear that if this domain boundary energy arising from the exchange force is greater than the demagnetization energy of the single domain, the element will be a single domain uniformly magnetized This condition is fulfilled for an element of any material below a given size depending on shape For a sphere of iron the limiting diameter is of the order of 10^{-6} cm For a prolate ellipsoid the long axis of the limiting size becomes longer the greater the axial ratio Consider now a material consisting of a non-magnetic matrix in which are embedded magnetic inclusions If the included particles are below the critical size for single domains we have a material in which each domain is isolated and no domain boundary movements can take place The only change in magnetization which can occur is that due to rotations within the domains If such particles have an anisotropy of shape, crystal energy, or stress there exists a critical field at which rotations are irreversible and the average coercive force can be calculated as

$$H_c \simeq \frac{F_a}{J_s} \tag{6}$$

where F_a is the energy associated with the anisotropy *i e* the energy required to rotate the magnetization from an easy into a difficult direction

For stresses, crystal anisotropy and ellopsoidal shape anisotropy only, F_a becomes respectively F_σ, F_k and F_{sh}, where

$$\left.\begin{aligned} F_\sigma &= \tfrac{3}{2}\lambda\sigma \\ F_k &= K \\ F_{sh} &= \tfrac{1}{2}(N_b \quad N_a) J_s^2 \end{aligned}\right\} \tag{7}$$

N_b and N_a being the demagnetization factors along the short and long axes respectively ,

Inserting any of these values in equation 6 we obtain values for the maximum coercive force , the difference between that theoretical maximum and the actual value gives a measure of the relative importance of domain boundary movements compared with rotations of domain magnetization

Results of experiments on iron-nickel-aluminium magnet alloys suggest that these alloys in their fully heat treated condition are in a state of heterogeneity in which there are magnetic islands, probably of single domain particle size, with a strong cubic anisotropy , these are not surrounded by non-magnetic, but rather by more weakly magnetic, material The high coercive force found in these materials is probably mainly due to the fact that boundary movements play a secondary role while rotations of magnetization are of primary importance A material of this kind can be quite adequately described by a slight modification of Néel's theory, introducing some of Stoner and Wohlfarth's ideas

On the basis of such a model[7] it is also possible to understand the directionally anisotropic properties of a magnet of one of the recent materials which are heat treated in a magnetic field to increase the energy product in a chosen direction

EXPERIMENTS MADE IN THE CENTRAL RESEARCH LABORATORY

In order to arrive at an interpretation of the high coercive force of permanent magnet alloys, and to decide which of the proposed models can best account for the observed magnetic hardness, it is necessary to know the actual values of all physical constants appearing in the theoretical expressions A search through existing literature has shown that very few published data are available, hence we have attempted to make such measurements as were required In the first place our experiments were limited to the explanation of coercive force, leaving directional treatment in a magnetic field out of account Hence all subsequent experiments refer to alloys which had been given the commercial heat treatment, without the application of a magnetic field This work is not yet complete, especially regarding measurements on some new alloys which have been recently added to the range of commercial permanent magnet materials

The first attempt was naturally to test the validity for magnetic alloys of the simple stress theory A J BRADLEY and A TAYLOR[8] found in their x-ray investigation of the iron-nickel-aluminium system that alloys near the composition Fe_2NiAl are single phase at high temperatures, separating into two body centred cubic phases with nearly equal lattice parameter at low temperatures. Hence it was suggested by these authors that during the controlled cooling given to commercial magnet alloys the precipitation process was initiated: small islands of the second phase were formed but did not break away from the parent lattice, thus setting up great stresses.

Experiments were therefore carried out on Fe_2NiAl, which is almost identical with the commercial alloy known under the name of *Alni*.

An alloy of 27·9 per cent nickel, 12·67 per cent aluminium and the rest iron was prepared, and the heat treatment developing maximum magnetic hardness was applied. After this treatment the coercive force was 454 oersted.

The product $\lambda_s \zeta_i$ can, according to Becker's theory, be determined from measurements of the initial susceptibility; this gave $\lambda_s \zeta_i = 3{\cdot}62 \times 10^5$ erg. The value of saturation magnetization could be measured as $J_s = 680$ c.g.s. units.

Thus according to equation 1 p_1 would be 0·85, *i.e.* it would be of the expected magnitude.

However the magnetostriction constant λ_s is found to be only about 6×10^{-6}, hence ζ_i would have to be 6×10^{10} dynes/sq cm (in practical units 600 kg/sq mm, or 380 ton/sq in) a value which is far in excess of what could be assumed as reasonable. Hence it did not appear likely that the simple stress theory was applicable here.

In a fully treated sample of *Alcomax II* alloy (nominal composition 11 per cent nickel, 21–24 per cent cobalt, 4–6 per cent copper, 8 per cent aluminium) the initial susceptibility indicated a $\lambda_s \zeta_i$ value of $7{\cdot}32 \times 10^5$ erg, J_s being 1,075 c.g.s. units. With a coercivity $H_c = 510$ oersted p_1 would be 0·75 *i.e.* again of the required magnitude. In this instance the magnetostriction is fairly large, λ_s (isotropic) $= 20 \times 10^{-6}$, giving $\zeta_i = 3{\cdot}7 \times 10^{10}$ dyne/sq cm, a smaller value than in *Alni*, but still 370 kg/sq mm (240 ton/sq in). Thus in *Alcomax II* the calculated microstress is approaching a practicable value, and another critical experiment was performed.

If the stress model is correct then ζ_i can be deduced from the change in remanence when a homogeneous stress is applied. The experiment was carried out on a sample of hardened *Alcomax II*, giving ζ_i about twice the value derived from measurements of initial susceptibility and saturation magnetostriction.

Bearing in mind the essential similarity of all aluminium-nickel type magnet alloys it appears that the simple stress model is not adequate to describe the origin of their coercive force.

The inclusion model of Kersten was ruled out, because detailed microscope studies did not reveal any large non-magnetic inclusions in any of the alloys.

Furthermore, if the non-magnetic inclusions are not visible there is no direct method of measuring the actual volume occupied by them, and since their shape is also unknown a comparison with theory which would be at all significant is not possible.

However, there is indication of a more or less periodic change in composition throughout the lattice, and the periodicity appears to be of the order of magnitude of the critical dimensions for single domain particles, 10^{-4} to 10^{-6} cm. (A peculiarly regular pattern could be observed in the microstructure under the highest optical magnifications. Electronmicrographs kindly taken by Dr J. NUTTING, Cavendish Laboratory, Cambridge, whilst being inconclusive because of technical difficulties, appear to give a microstructure of a particle size, or periodicity, of 10^{-4} to 10^{-6} cm.) Hence whilst we cannot have isolated magnetic islands, as required in Stoner and Wohlfarth's single domain model, there is possibly a variation in intrinsic magnetization as envisaged by Néel. This view is supported by detailed inspection of J_s against T and dJ_s/dH against T curves, showing that the alloys do not possess one sharp Curie point, but that there is a more gradual decrease in magnetization than in pure metals or single phase alloys.

Consequently it was necessary to measure the crystal energy K and the root mean square $\bar{J}_s$ of the magnetization, see equation 4.

Approximate measurements of $\bar{J}_s$ can be made from the approach to saturation curve, and this was done for *Alcomax II*, *Alcomax IV* and *Hycomax* alloys, all of which belong to the iron-nickel-aluminium-cobalt-copper group of alloys with individual variations in composition and treatment.

If single crystals are not available the magnetocrystalline energy K can be found in stress free materials, either from the approach to saturation or from the reversible energy of magnetization. In our alloys the conditions of being stress free is certainly not fulfilled, but a study of the magnetostriction properties[8] of these alloys showed that the anisotropy (even if not due to crystal forces only but also to heterogeneity, stresses, or a superposition of all these causes) is essentially of the same symmetry as the crystal lattice, hence we can measure a quasi-crystal energy K' in which the contributing causes cannot be separated.

Only preliminary measurements of K' have so far been carried out, and these, together with some approximate values of $\bar{J}_s$ used in equation 4 appear to give good agreement with the measured H_c for *Alcomax II* and *Hycomax*

The calculated coercivities are shown in *Table I* and are compared with measured values of the same alloys, not necessarily taken from the same cast

Table I

Comparison of Experimental and Theoretical Values of Coercive Forces in some Permanent Magnet Alloys

Alloy	*Coercive force H_c oersted*	
	Measured	*Calculated from equation 4*
Isotropic Alcomax II		
hardened only	253	200
fully treated	510	450
Isotropic Hycomax		
hardened only	—	406
fully treated	720–750	8 6
Isotropic Alcomax IV		
hardened only	120–130	188
fully treated	590	843

With *Alcomax IV* the agreement is very unsatisfactory, but it was found that the particular sample used was not representative of a polycrystalline material, in that it had mainly unidirectional rather than randomly orientated crystals In that instance it is clear that measurements of K' might differ from the true value by a large factor

The original method of measuring the approach to saturation and the reversible energy of magnetization which provided the data necessary for the calculations was not satisfactory A more accurate method has been devised and a detailed study of a great number of permanent magnet alloys is at present in progress

The agreement between theory and experiment found in some alloys so far justifies the hope that the proposed mechanism is indeed the major factor contributing to the magnetic hardness

Thus it is gratifying to find that the very high coercive forces and stored energy $(BH)_{max}$ of modern permanent magnet alloys does not have to be explained by variations in the energy of domain boundaries, which occupy only a small fraction of the total volume The cause for the measured properties resides rather in the bulk of the material These conditions are expressed in some way by the very high values found for K', the quasi-crystal anisotropy (1×10^6 to 2×10^6 erg/cc) and by the high degree of magnetic heterogeneity ($\bar{J}_s = 1\ 10\ J_s$ to $1\ 20\ J_s$)[7] The simultaneous study of the origin of the magnetic anisotropy of some of these alloys produced by the cooling in a magnetic field has also yielded valuable results published elsewhere[9] so that it is not unreasonable to hope that a complete and comprehensive picture of the elementary processes responsible for the remarkable properties of modern iron-nickel-aluminium type permanent magnet alloys will be arrived at

I wish to express my thanks to Dr M McCaig of the Permanent Magnet Association, who has carried out most of the experimental measurements referred to in this review, for constant advice and valuable discussions, and to the Permanent Magnet Association for permission to publish this account

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Miscellaneous Notes

NEW YEAR HONOURS

THE New Year Honours list issued on 1 January 1950 included the following

Knight Bachelor— Professor A G TANSLEY, Chairman, Nature Conservancy

K B E — F BRUNDRETT, Chief of the Royal Naval Scientific Service.

ROYAL SOCIETY

The President of the Royal Society has appointed the following Vice-Presidents for the ensuing year .

Sir THOMAS MERTON— Treasurer of the Royal Society

Sir EDWARD SALISBURY, C B E — Biological Secretary of the Royal Society , Director of the Royal Botanic Gardens, Kew

SIR DAVID BRUNT—Physical Secretary of the Royal Society, Professor of Meteorology, Imperial College of Science and Technology

Professor C E TILLEY—Professor of Mineralogy and Petrology, University of Cambridge

APPOINTMENTS

London University—Dr E H BALDWIN has been appointed to the University Chair of Biochemistry, tenable at University College from 1 January

Professor H E M BARLOW, Professor of Electrical Engineering at University College, has been appointed to the Pender Chair of Electrical Engineering, tenable at the College from 1 October 1950 He succeeds Professor R O KAPP who is retiring at the end of the 1949–50 session

The title of Professor of Chemistry in the University has been conferred on Dr K LONSDALE, F R S, in respect of the post held by her at University College

The title of Professor of Aeronautical Engineering in the University has been conferred on Dr N A V PIERCY in respect of the post held by him at Queen Mary College

Manchester University—Professor C W WARDLAW has been appointed Dean of the Faculty of Science

Commonwealth Bureau of Dairy Science, Reading—A W MARSDEN has been appointed Director of the Bureau and took up his duties on 1 January

Commonwealth Scientific and Industrial Research Organization, Australia—Two new chiefs of C S I R O Divisions have been appointed Dr W BOAS succeeds Dr S H BASTOW as chief of the Division of Tribophysics and F J LEHANY succeeds Dr D M MYERS as Chief of the Division of Electrotechnology a unit of the National Standards Laboratory

ADAMS PRIZE

This Prize, offered by the University of Cambridge for an essay on a mathematical, astronomical, or natural philosophical subject, has been awarded equally to Dr J C BURKILL, Cambridge, Dr S CHANDRASEKHAR, Chicago, H W HAYMAN, Exeter, and Professor J M WHITTAKER, Liverpool

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, AUSTRALIA

Wool is of the utmost importance to Australia, being its major export and allowing the use of marginal land In developing the programme of agricultural research C S I R O has been concerned with soil, plant and animal aspects of the growth of wool

Soil fertility is of prime importance and outstanding results have been achieved in combating soil infertility arising from minor element deficiencies On the plant side, too, special emphasis has been placed on pasture investigations and on weed control

Further study has been made of the limitations imposed on the health and productivity of animals and plants by deficiencies of cobalt, copper, zinc *etc* Special attention has been paid to the effects that the chronic ingestion of molybdenum has on copper metabolism Results of the research carried on show that ingestion of moderate amounts of molybdenum hasten the effects of copper deficiency in sheep on copper deficient pastures

Other aspects of the problem considered include the effect of nutrition on wool production, processes of rumination, energy metabolism, vitamin requirements, genetical studies, diseases and parasites

SPECTROCHIMICA ACTA

The publication of *Spectrochimica Acta* has been taken over by Butterworth-Springer Ltd, and the first number of the fourth volume will appear shortly under the new imprint The first two volumes of the journal were published by Springer-Verlag, Berlin, to provide an international medium of publication for papers on emission and absorption spectroscopy applied to analysis, and on the physics of light sources A third volume was published in 1947–8 jointly by the Vatican Press, Castel Gandolfo, with Springer-Verlag, Heidelberg

The Editorial Board consists of representatives of the United Kingdom, the U S A, France, Belgium Germany, Italy and Spain Papers will be published as hitherto in English French and German Contributions in English should be sent to E H S VAN SOMEREN, at 4 Churchfields, Broxbourne, Herts

ENDEAVOUR PRIZES

Imperial Chemical Industries Ltd, publishers of *Endeavour*, have offered the sum of 85 gns to be awarded as prizes for essays on a scientific subject The main purposes of the awards are to stimulate younger scientists to take an interest in the British Association for the Advancement of Science, and to raise the literary standard of scientific writing The competition is limited to those who are not more than 25 years of age on 25 June 1950 Full particulars may be obtained from the Assistant Secretary, British Association for the Advancement of Science, Burlington House, Piccadilly, London, W 1

CORRECTION

On p 39, line 7 of the left hand column should read :

$$\mathcal{N}(x) = \Phi(x) - \tfrac{1}{2}[\theta(x) + 1] = \frac{1}{\pi^{\frac{1}{2}}}\int_0^x \exp(-x^2)\,dx + \tfrac{1}{2}$$

New Books

Elektrische Wellen

W O SCHUMANN
(*340 pp, 248 illus, 9½ in by 6½ in*)
Munich Carl Hanser Verlag, 1948 *DM*28 50

Pulses and Transients in Communication Circuits

C CHERRY
(*xvi + 317 pp, 129 illus, 8½ in by 5½ in*)
London Chapman and Hall Ltd, 1949 32*s* net

Waveforms, M I T Series, Vol XIX

Edited by B CHANCE, I C WILLIAMS, V HUGHES, E F MACNICHOL and D SAYRE
(*xxii + 785 pp, illus, 9 in by 6 in*)
New York McGraw-Hill Publishing Co Inc, 1949
$10 00
London McGraw-Hill Publishing Co Ltd, 1949 85*s*

THESE three books together present a comprehensive and practically exhaustive account of theoretical and practical aspects of electric waves Professor W O SCHUMANN's book is entirely theoretical and gives a thorough mathematical analysis of the various types of electromagnetic waves, C CHERRY's book is, as the subtitle says, 'An Introduction to Network Transient Analysis for Television and Radar Engineers', and the book on Waveforms describes the practical details of generating and applying voltage and current waves of various shapes and durations

In *Elektrische Wellen* the basic mathematical and electrical facts are presented in the first three chapters Then plane waves in dielectrics and conductors are considered Reflection of electromagnetic waves is studied in detail and the theory of wave propagation in media with free electrons is developed, application is made to the ionosphere A large section of the book is devoted to the types of waves which are possible within waveguides of various cross sections The book concludes with an account of spherical waves and the reciprocity theorem for electric waves For those who appreciate visual pictures of the properties of electric waves there is a profusion of excellent diagrams, lines of electric and magnetic force being drawn for every type of wave studied References to the literature might have been more extensive and, in particular, various important British and American papers of recent years are not mentioned (presumably not available in Germany)

In *Pulses and Transients in Communication Circuits* the aim has been to use rigorous physical arguments but only elementary mathematics It is well known that the theory of transients involves, in its proper treatment, more difficult mathematics than the theory of the steady state But in this book the author has avoided the operational calculus and the treatment is largely 'geometrical', or pictorial, rather than analytical After an introductory chapter the frequency spectra of modulated waves, pulses and transients are considered Then the transient response of networks is discussed One chapter is devoted to characteristics of multi-stage amplifiers, one to asymmetric sideband channels and another to reflection and echo effects in lines and in lumped networks The book should be popular among television and radar engineers For those whose interest is more in the mathematics of transients the book will be, at most, introductory

Waveforms is volume 19 of the Radiation Laboratory Series emanating from the Massachusetts Institute of Technology It is an encyclopaedic work, packed with details of many kinds of circuits for producing various waveforms both fundamentals and applications receive considerable emphasis An outline of the contents will show the breadth of the field covered

The book commences with details of operations on waveforms with linear or non-linear circuit elements Various types of modulation and demodulation are considered and the characteristics of non-linear circuit elements are discussed Over fifty pages are devoted to sinusoidal waveform generators, including crystal oscillators, phase shift oscillators, bridge oscillators, negative resistance oscillators and beat frequency oscillators Methods for stabilizing oscillators are considered and the generation of pulsed sinusoidal oscillations by means of the Hartley or crystal oscillator is described The generation of *abrupt* waveforms (called fast waveforms) is described in the next chapter Multivibrators and phantastron-type circuits may be used and full details of these are given Particulars of the sanatron and sanaphant circuits, developed a few years ago, are included The generation of waveforms by blocking oscillators and delay-line pulse generators is also discussed Finally a description is given of methods for generating triangular and special waveforms, such as exponentials and hyperbolas The next section of the book is devoted to methods for operating upon waveforms Amplitude, selection, comparison and discrimination are discussed, and there is a chapter on time selection Several chapters are devoted to modulation and demodulation, and a chapter on electromechanical modulators is included

Two chapters are given to a description of methods for achieving frequency multiplication and division. These lead to the chapter on counting, sequence circuits and energy storage counters are described The next two chapters, dealing with mathematical operations on waveforms, describe what must be the highlight in the development of the uses of waveforms in recent years Circuits for addition and subtraction, or for differentiation and integration, are described Next come circuits for multiplication and division, and for forming squares and square roots All these are applicable in electronic computing devices, which have been developed both in Great Britain and America The book closes with chapters on electrical and supersonic delay devices

From this survey of the contents it will be noticed that practically all that there is to be said about waveforms is said in this book It will surely be a necessary book in any library which covers radio and electrical engineering

J S GODDARD

Trattato di Fisica Generale e Sperimentale

Sixth Italian edition E PERUCCA

(*xxiv + 802 pp, 713 illus, 9¾ in by 7 in*)

Turin Unione Tipografico-Editrice Torinese 1949
IL 5,500

THE continuous progress of physics with numerous discoveries of new methods and experimental procedures makes it very difficult to write a complete treatise in this field The present work must be considered, however, a successful attempt to cover the enormous ground of experimental physics in its development from its origin to its present state

Despite the enormous number of experiments the author has had to describe he has succeeded in allotting a considerable part of the book to the fundamental concepts of the classical theories He has found room for the flux theorem of GAUSS in field theory, for CAUCHY's stress theorem in the mechanics of deformable bodies, and for the GIBBS-HELMHOLTZ equation and principles of kinetic theory of gases in thermodynamics The result is a book which is useful not only to undergraduates but also to the more advanced research workers in any branch of the natural sciences for whom the methods used in physics might be a source of valuable suggestions

The first volume, the sixth edition of which has recently been printed, deals with Mechanics and Heat The first chapter gives a detailed description of the fundamental physical instruments and the definitions of fundamental units The second introduces the concept of vector, and gives the fundamentals of vectorial calculus The kinematics of a particle is extensively treated, and particular attention is paid to the composition of motions and to harmonic motions Only a few pages are devoted to the kinematics of a rigid body

In Statics one chapter is devoted to theorems of field theory, such as those of GAUSS and STOKES, and to the definitions of conservative systems of forces Several examples of simple problems of the statics of a particle and the statics of systems of particles are given In a similar way the author deals with Dynamics, many of the classical experiments (GRIMSEHL's, FLETCHER's LABORDE-NEUMANN's, ATWOOD's *etc*) being described in detail The study of newtonian fields of forces, of the earth's gravitational field, and a description of CAVENDISH's and FOUCAULT's experiments follows

The second part contains a few basic ideas on the constitution of matter structure of crystals elasticity and mechanics of fluids The third part on acoustics, is devoted to the theory of waves in an elastic medium, and to a description of the most important acoustic instruments and their technical applications

The final part is concerned with thermometry, calorimetry, and the three principles of thermodynamics Several theoretical consequences of these principles, and many important formulae such as GIBBS-HELMHOLTZ', KIRCHHOFF's specific heats equation, STEVINO's and HENRY's laws are discussed in detail At the end there are a few basic ideas on the kinetic theory of gases, and on the production of high vacua

This is a book which will be very useful both for reference for the research worker, and as a guide for the student It is remarkably complete and should be considered outstanding equal to almost any other work of the same kind which has so far been published

C FRANZINETTI

Books to Come

Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmechanik P GOMBÁS (*266 pp 20 illus*) Basel Verlag Birkhauser *Fr 29 50*

Index of Nomograms *Edited and compiled by* D P ADAMS (*174 pp*) New York John Wiley and Sons Inc *c $5 50*

Classical Mechanics D E RUTHERFORD (*212 pp, crown 8vo*) Edinburgh Oliver and Boyd Ltd *c 10s 6d net*

Manual of Physics, *Fifth edition* J A CROWTHER (*616 pp, crown 8vo*) London Oxford University Press *c 21s net*

The Chemistry of Uranium *Edited by* J J KATZ and E RABINOWITCH New York and London McGraw-Hill Book Company Inc

Analytical Absorption Spectroscopy *Edited by* M G MELLON (*c 495 pp 200 illus*) New York John Wiley and Sons Inc *c $9 00*

RESEARCH SUPPLEMENT

Envelopes of Oil Drops Suspended in Glue Solution

S MATHEWS, M Sc, A R C Sc, A Inst P

The oil/glue solution interface was studied by the elongated pendent drop shape method Interfacial and membrane tensions were deduced from the shape of the pendent drop The solid nature of the mature linseed oil/glue solution membrane was established

In 1941 the shortage of materials for camouflage paints and the anomalous behaviour of some pigments in linseed oil/glue solution emulsions resulted in the study of the fundamental properties of such emulsions Microscopic examination of paraffin/glue solution and linseed oil/glue solution emulsions, with and without pigment, revealed that, whereas all the paraffin droplets remained spherical after collision, the larger of the linseed oil droplets suffered permanent distortion This suggested that the physical properties of the surfaces of the linseed oil droplets were not as simple as those of an ordinary liquid/liquid interface

Oil/water interfaces were investigated before complicating the issue by adding glue, which reduces boundary tension by virtue of the adsorption of its large molecules near the surface of an aqueous solution The linseed oil/water interfacial tension was measured, first by the capillary tube and cups method[1], then by balancing a small spherical drop against a measured hydrostatic head[2], the results are given in *Table III*, p 88 These methods however, were found inapplicable to the linseed oil/glue solution interface because adsorption caused meniscus creep in the first method and detachment of the drop in the other, so the elongated pendent drop shape method, using wide jets, was chosen, as it provides extensive anchorage Incidentally it also gives opportunities for controlling and examining the envelope of a drop

Analysis of pendent drop shape as published by Bashforth and Adams[3] [illegible] 1883, two years after Worthington's[4] observations, involves considerable mathematical labour Tables published by Andreas, Hauser and Tucker[5] in 1938 were therefore used these give boundary tension in terms of two diameters of the drop The phrase ' boundary tension ' covers surface tension, interfacial tension, or any tension in the envelope of the pendent drop The following account describes determinations carried out with an ordinary microscope and depending on the observer's ability to estimate one tenth of a division of the micrometer eyepiece squares The deviation from the mean value found for an interfacial tension by this method and from the values obtained by the author using other methods seldom exceeded five per cent, published results for low interfacial tensions sometimes differ by as much as fifteen per cent

The beauty of the pendent drop shape method is that low boundary tensions do not diminish accuracy of measurement Other advantages are

1 there is only one interface under consideration hence contact angles do not enter into the measurements

2 changes in interfacial tension can be studied without breaking the interface or moving its anchorage

3 a clean interface can readily be formed

4 measurements are performed on the interface only and not on remote liquid levels

5 low density difference between the phases increases accuracy of drop shape evaluation

The relative adhesions of two liquids to the same solid can be determined by noting whether the drop is pendent from the external or the internal circumference of the jet

BOUNDARY TENSION DEDUCED FROM PENDENT DROP SHAPE

The boundary tension of a drop can be evaluated by measuring the equatorial diameter and the diameter of a selected plane the distance of which from the pole of the drop is equal to the equatorial diameter, using the formula

$$\gamma = \frac{(\varrho_1 - \varrho_2)\, g\, d_e^2}{H},$$

where γ is the boundary tension in dynes/cm, ϱ_1 and ϱ_2 are the densities of the two phases in gm/cm, g is the acceleration due to gravity, d_e the equatorial diameter of drop in cm and $H = \beta\,(d_e/b)^2$, where β depends on the coordinates and radius of curvature at any given point on the profile and on the angle made with the horizontal by a tangent at that point, and b is the radius of curvature at the pole, from this can be derived an expression which involves d_s, the diameter of the plane the distance of which from the pole is equal to the equatorial diameter

Andreas, Hauser and Tucker's empirically compiled tables give $1/H$ versus d_s/d_e A method of calculating the relationship between $1/H$ and d_s/d_e has been published, with tables, by FORDHAM[6], but the values do not deviate from those in the empirical tables by more than 1½ per cent

It is necessary that the drop should be elongated, so that d_s/d_e is at least 0 7 before the tables can be applied To obtain elongated drods the diameter of the jet must be chosen to suit the interfacial tension and the buoyancy of the drops

APPARATUS

Since the oil was lighter than the glue solution a 'pendent' drop of oil was obtained by bending the tube from which it emerged so that the orifice pointed upwards, *Figure 1*, but for glue solution drops pendent in oil straight tubes were used

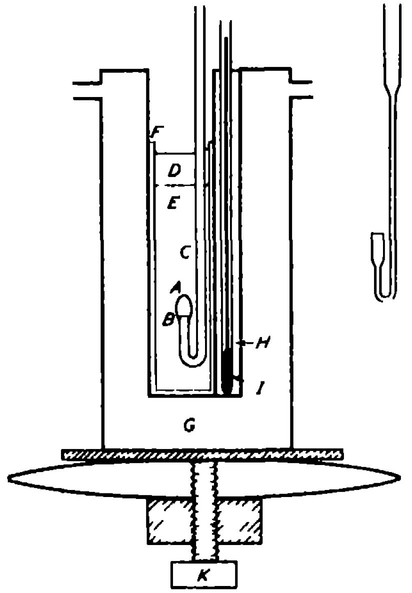

Figure 1 Section through tube C supporting oil drop A at its orifice B surrounded by aqueous phase E contained in parallel-sided glass cell F

Inset Shape of tube for large jet diameters

A layer of oil D covered the surface of the aqueous phase This prevented evaporation and provided a reservoir from which the tube could be replenished To ensure cleanliness of the interface at the beginning of each experiment a few drops of oil were expelled through the orifice before adjusting the hydrostatic pressure so that the pendent drop was the shape required there was no difficulty in maintaining the right shape for an indefinite period provided the jet was of suitable diameter and material

The glass cell *F* was partially enclosed by a water jacket *G* which left two sides exposed, through which the drop was observed microscopically One side of the jacket was recessed at *H* and accommodated a thermometer *I* close to the cell, the latter being too small to hold the thermometer as well as the J-tube It was shown that the temperatures inside the cell and recess differed by less than ½C° the latter being constant to within ½C° The hydrostatic pressure governing drop shape was varied by altering screw *K*, or by withdrawing oil from the tube using a fine pipette

Different objectives were used according to the size of drop, and the micrometer eyepiece (ruled in squares) was calibrated for each objective The drop profile was copied on graph paper

Choice of diameter and material of jet— If the jet is too small the drop will remain spherical however the pressure is altered, and if the jet is too large the drop will not have an equator until it detaches For the higher interfacial tensions the jet diameters were large and the glass J-tubes had to be drawn into capillaries near the bend (see inset to *Figure 1*) to allow space within the cell for the oil drop

So long as the boundary tension of the drop was greater than 1 dyne/cm, glass tubes could be used whatever the relative wetting powers of the liquids, but when a linseed oil drop was left suspended in glue solution its boundary tension fell practically to zero as the adsorbed glue envelope congealed, and while this envelope was still semifluid the glue solution ousted the oil at the margin where the drop was anchored, so the drop detached itself before a membrane was consolidated Therefore it was necessary to use a clean metal tube for anchoring linseed oil drops in glue solution while maturing membranes

Specification of materials investigated— Fireproof thinner was added to the glue solution to comply with the usual specifications for such emulsions, and measurements with a Du Noüy tensiometer showed that this had no effect on the surface tension for concentrations between 6 5 and 1 per cent glue, which remained steady at 37 5 dynes/cm Dilution to a concentration of 0 1 per cent glue raised the

Table I Specification of Materials

Name	*Description*
1 per cent glue solution	*1 gm cascade glue dissolved in 99 gm distilled water below 50°C, used fresh*
Cascade glue	*pH = 5 73 ± 0 02 for a 5 per cent solution*
Varnish linseed oil	*At 21°C, density 0 926, refractive index 1 4796, acid value 9*
Medicinal paraffin	*At 21°C, density 0 880 refractive index 1 4819*
Fireproof thinner	*Mono-ammonium phosphate solution neutralized with ammonia, and water added so that solids content = 12½ per cent*

Table II Surface Tensions of Specified Materials

Liquid	*Surface tension dynes/cm*	*Temp °C*	*Density gm/cc*	*Method*
Water, distilled	72	20	0 998	*Capillary tube*
" "	72	20	0 998	*Tensiometer*
Varnish linseed oil	34	20	0 927	*Capillary tube*
" "	37	20	0 927	*Tensiometer*
Varnish linseed oil with 3 per cent litharge	31	20	0 947	*Capillary tube*
Medicinal paraffin	32	19	0 882	*Capillary tube*
" "	33	17	0 884	*Tensiometer*
Medicinal paraffin with 1 per cent oleic acid	35	19	0 883	*Tensiometer*

surface tension to 40 dynes/cm, and further dilution gave a solution having the same surface tension as pure water *viz* 72 dynes/cm

Since low interfacial and surface tensions of glue solutions are due to adsorption it is reasonable to suppose that this has reached saturation when the concentration is one per cent In pendent drop shape measurements any greater percentage of glue made observation of oil drops difficult owing to the greater scattering of light

EXPERIMENTAL RESULTS

Effect of adhesion between phases— Medicinal paraffin differs from linseed oil in that it is neutral and has a large interfacial tension against water Oleic acid was added to the paraffin so that its adhesion to water[7] might approach that of the linseed oil which contained polar acids, and the interfacial tension was then measured Experiments on raising the interfacial tension of linseed oil/water by adding litharge were also carried out *Table III* shows the results

These changes in interfacial tension are not accompanied by any appreciable effects on the surface tensions of the oils (*Table II*) showing that adsorption plays no part here in the lowering of the interfacial tensions, which must therefore be due to the attraction across the interface exerted by the water on the acids

When a linseed oil drop was left suspended in water for several hours its interfacial tension showed a decrease , after eighteen hours the interfacial tension was 4 6 dynes/cm, whereas after ½ hr the value was 5 6 dynes/cm at the same temperature In each instance the interface remained liquid

Reduction of boundary tension by glue adsorption— Drops of each of the oils were suspended in glue solution and then the reduced boundary tensions were measured (*Table IV*) There was a progressive change in the envelope of the drop , a freshly formed drop of oil had an ordinary liquid/liquid interface but after ½ hr the adsorbed glue started to gel A detailed examination of matured drops was therefore made

Paraffin drop suspended in one per cent glue solution— A pure medicinal paraffin drop was suspended in one per cent glue solution, elongated to the right shape for boundary tension measurements, and left undisturbed for at least ½ hr If subjected to slightly increased pressure it would detach in the same way as if it were in water This detachment occurred at a boundary tension of 15 dynes/cm whether the drop was ½ or 20 hr old

If the pressure was partially released the drop became cylindrical (profile 2, *Figure 2*) Measurement now indicated a boundary tension of 7 3 dynes/cm which increased steadily to 8 7 dynes/cm within ½ hr, and ½ hr later was 15 dynes/cm, the value characteristic of the paraffin/glue solution interface The pressure was again reduced, more suddenly this time, and folds appeared at the neck of the drop which assumed profile 3 , these smoothed out in the course of 10 min while the drop assumed a shape consistent with the equilibrium boundary tension The gelled envelope had slowly flowed until it fitted the drop's new volume and thus exhibited liquid qualities

Addition of oleic acid reduced the interfacial tension to 1 3 dynes/cm and greatly retarded the smoothing out of folds, but the envelope still behaved like a liquid and flowed evenly round the oil drop, unless it was subjected to sudden changes when it behaved like an elastic solid until its boundary tension reached 2 5 dynes/cm, after which it exhibited quasi-flow and detached at a boundary tension a little above 7 5 dynes/cm (*Figure 3*)

Linseed oil/glue solution interfaces between ½ and 4 hr old, using glass jets— Whereas a paraffin drop remained pendent from a glass jet in a glue solution in the shape appropriate to its interfacial tension of 15 dynes/

Table III Interfacial Tensions Oil/Water

Liquids	*Interfacial tension dynes/cm*	*Temp °C*	*Age of interface hr*	*Method*
Linseed oil/water	5 5 ± 0 3	17	*Uncertain*	*Capillary tube and cups*
" " "	5 5 ± 0 5	18	1	*Sessile spherical drop on capillary orifice supporting measured head in quill tube*
" " "	5 3 ± 0 5	19	24	*Pendent drop from capillary orifice supporting measured head in capillary tube*
" " "	5 6 ± 0 3	19	½	*Pendent drop shape*
Linseed oil with 3 per cent litharge/water	17	24	*Any from ½ to 2*	*Pendent drop shape*
Paraffin/water	46	21	"	*Pendent drop shape*
Paraffin with 1 per cent oleic acid/water	10	21	"	*Pendent drop shape*

Table IV Boundary Tensions, Oil/Glue Solution, from Pendent Drop Shape

Liquids forming interface	*Interfacial tension dynes/cm*	*Yield value of envelope dynes/cm*	*Temp °C*	*Age of interface hr*
Paraffin/1 per cent glue solution	15		21	½ *to* 20
Paraffin with 1 per cent oleic acid/1 per cent glue solution	1 3	2 5 *for sudden stress*	21	1½ *to* 20
Linseed oil/1 per cent solution	3 5		25	½ *to* 4
Linseed oil with 3 per cent litharge/1 per cent solution	6		25	1
Linseed oil modified by ageing/1 per cent glue solution	0	*Lower* 3 5 *Upper* 6 *to* 8	21	17 *to* 68

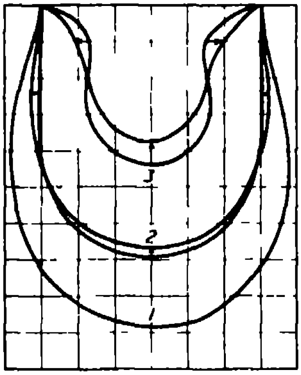

Figure 2. Paraffin drop pendent in 1 per cent glue solution at 21°C under various hydrostatic pressures. Scale: 1 micrometer eyepiece division = 0.069 cm.

Profile 1. Pressure adjusted to give this shape and left overnight. 20 hr caused no alteration. Boundary tension 15 dynes/cm.

Profile 2. Liquid withdrawn from drop. Elastic after-effect indicated by arrows.

Profile 3. Pressure further reduced and folds appear at neck; these smooth out within 10 min while drop assumes shape having higher boundary tension.

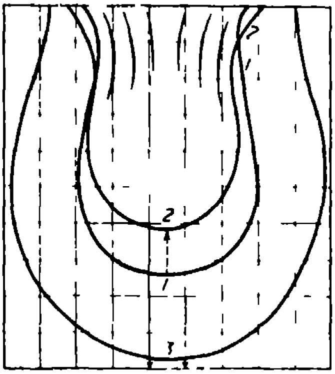

Figure 3. Paraffin with 1 per cent oleic acid/1 per cent glue solution at 21°C. Scale: 1 micrometer eyepiece division = 0.0805 cm.

Profile 1. Pressure adjusted to produce folds and left overnight.

Profile 2. Envelope 20 hr old, folds smoothed out overnight; boundary tension = 1.3 dynes/cm.

Profile 3. Internal pressure steadily increased and drop profile plotted at intervals, showing maximum boundary tension (7.5 dynes/cm), for which the drop did not expand while its shape was being plotted.

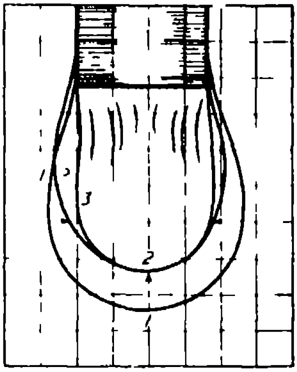

Figure 4. Linseed oil drop pendent from metal jet in 1 per cent glue solution at 21°C. Scale: 1 micrometer eyepiece division = 0.069 cm.

Profile 1. 20 hr old membrane subjected to internal pressure which produces boundary tension = 5.8 dynes/cm.

Profile 2. Same membrane 48 hr later, having relaxed until drop shape indicates boundary tension = 3.3 dynes/cm.

Profile 3. Result of reducing internal pressure. Folds appear which do not smooth out with lapse of time.

cm, a linseed oil drop always elongated within a few hours to a shape consistent with zero interfacial tension and detached itself. Therefore, all measurements on linseed oil drops on glass jets were made within four hours of their formation.

During the first ½ hr adsorption caused the interfacial tension to fall so rapidly that it was impossible to plot the drop shape. Striking changes occur in the elastic properties of the interface. If a drop is allowed to emerge and grow rapidly to twice the diameter of the orifice it can be made to retreat into the tube if the pressure in the external phase is increased within the first few minutes; the radius at the equator can be reduced at about the same rate as that at the pole and the drop preserves its sphericity while retreating. This will occur with any liquid/liquid interface.

If an attempt is made to drive the drop back when the interface is more than ½ hr old the increased external pressure will merely flatten the sides since the interface is no longer mobile. Further increase of external pressure causes a neck to form, and eventually its sides unite and the drop detaches, showing that the envelope is a gel with a very low yield value.

When a drop with a liquid/liquid interface is expanded, however, the drop becomes so large that its buoyancy pulls it into an unstable cylindrical shape, and if a linseed oil drop in a glue solution is over expanded it will behave in this way because excess tension makes it yield.

When a drop was not allowed to emerge past the hemispherical shape it was possible to drive it back even after the first ½ hr, though it was necessary to increase the external pressure slowly and allow for lag in the contracting envelope.

Boundary tension measurements on drops of any age between ½ and 4 hr all gave the value 3.5 ± 0.2 dynes/cm for linseed oil in glue solution (*Table IV*).

Membrane formation by matured linseed oil/glue solution interfaces—Glue solution drops suspended from straight glass tubes in linseed oil when several hours old behaved as if enveloped by solid membranes. But in order to keep a linseed oil drop pendent in glue solution with the jet projecting well into the drop it was necessary to use a tube preferentially wet by the oil. A clean brass J tube was therefore used for maturing the envelopes of linseed oil drops.

Profiles of several drops were plotted for membranes between one and three days old. A membrane over 17 hr old, attached to a jet preferentially wet by the internal phase, yielded at boundary tensions between 6·5 and 7·3 dynes/cm , the older the drop the greater the boundary tension attained before it detached on increased internal pressure

When maturing a membrane for over 24 hr it was best during the first 20 hr (both with glue solution in glass tubes and linseed oil in metal tubes) to let the end of the tube touch the surface of the drop near the pole, so that the membrane had an extra line of support[8] The drop was then pushed to the end of the jet, and kept with its pole at a distance from the orifice equal to the equatorial diameter for another 24 hr, to consolidate the membrane near the neck, and then investigated

DISCUSSION OF PHYSICAL STATE OF INTERFACIAL MEMBRANE

It was found that the boundary tension in a mature linseed oil/glue solution membrane which had been at rest for 24 hr was always 3·5 ± 0·2 dynes/cm, if the membrane had been left with a tension equal to or above this value (*Figure 4*) Lower tensions in a mature membrane remained unchanged

On reducing the internal pressure the membrane behaved like a perfectly elastic solid for boundary tensions between 3·5 and 2 dynes/cm, but at this point folds appeared at the neck Increasing the internal pressure so that the boundary tension exceeded 3·5 dynes/cm caused extra stretching near the neck, and release of pressure allowed elastic return to a lower boundary tension , if the membrane were left without this release it relaxed until the drop assumed the shape characteristic of $\gamma = 3{\cdot}5$ dynes/cm

The only linseed oil drop still pendent from a ground glass orifice after standing overnight had its membrane hanging in folds, which smoothed out when the boundary tension was increased This behaved like a uniform elastic solid up to a tension of 5·6 dynes/cm when it yielded

A linseed oil/glue solution membrane can be matured as either a long or a short sack, and while it is elastic it maintains its original shape , this is shown by a membrane matured partly on a nearly hemispherical drop and partly on a thin layer of oil which covered the outside of the jet But the best shape of membrane for boundary tension determination is one formed on a drop with its selected plane level with the orifice of the jet which projects into the drop

CONCLUSION

The solid nature of the mature linseed oil/glue solution membrane, so long as it is not stretched beyond its elastic limit, is confirmed by the following facts when a pendent drop is left under reduced pressure so that there are folds in the neck its envelope does not flow and there is no detachment of the drop , a membrane formed on a certain shape retains this shape even when expanded , stress in the membrane is proportional to the internal pressure tending to expand the drop , and rough edges can be seen when the membrane is ruptured

This membrane appears similar to those formed with cod-liver oil in gum or gelatin solutions[9], and contrasts with the envelopes round olive oil, castor oil and mineral oil such as paraffin It also appears physically similar to each surface of the membrane of a living cell, where the outer layers consist of protein molecules lying on inner layers of fat[10, 11] Recent work on such membranes includes study of the stability of films consisting of fatty acid, monoglyceride and bile salt[12] following the work of Rideal and Schulman[13, 14], and study of the influence of colloidal electrolytes on the activity of drugs[15] , and Alexander[16] has recently mentioned the skin-like surface of oil droplets in emulsions Thus it is possible that the pendent drop shape method of measuring boundary tension might be of use in biophysics as well as in industrial physical chemistry

ACKNOWLEDGEMENTS

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Measurements on Enlargements on Plates and the Construction of a New Type of Photoelectric Granularity Meter

R DEBOT, Dr Sc

The first part of this paper describes the results of measurements of the statistical distribution of the local fluctuations in transparency and density in photographic enlargements Discussion of the results shows that accurate relationships exist between measurements of granularity based on one or other quantity, the variations of which are analysed Previously published theoretical formulae are very well verified It is further pointed out that it is necessary to measure the granularity around a large number of points on the granular test strip since individual measurements scatter widely, due not to a lack of reproducibility inherent in the methods used, but to the nature of the subject under investigation Since these measurements take a long time, the requirements are difficult to fulfil with present day methods The second part of the paper describes a photoelectric granularity meter which gives directly values of the mean square deviation σ_T of the transparency The apparatus works rapidly thereby allowing a sufficient number of measurements to be carried out, furthermore, the apparatus is universal in that it will determine σ_T values from 0 5 to around 0 01, for scanning spots with diameters which can be varied from 3 5 μ to several mm It can thus be used for measurements on an original plate as easily as for measurements on an enlargement

EXPERIMENTAL RESULTS

Introduction – In a previous paper[1] the method and apparatus have been described by which various magnitudes entering into the measurement and calculation of granularity can be determined Those methods and arguments which relate to density fluctuations were developed specially, but the transparency can be studied in a practically identical manner In particular, one can split up $\sigma(\Delta T/T)$ into $\sigma_+(\Delta T/T)$ and $\sigma_-(\Delta T/T)$ in the same way that $\sigma(\Delta D)$ was divided into $\sigma_-(\Delta D)$ and $\sigma_+(\Delta D)$ In a letter to the same journal[2] a simplified nomenclature i e σ_T, σ_{+T}, σ_{-T}, σ_D, σ_{-D}, σ_{+D}, has been proposed and will be used below

For a negative emulsion enlargements have been chosen from sensitometric steps numbered 1 to 5 in increasing order of density, picked so as to fall on that part of the characteristic curve which is utilized in practice[3] The step wedges were developed in two quite different types of developer, the first in a normal methol-hydroquinone developer for a time necessary to reach maximum gamma, the second in a fine-grain developer giving very soft gradation The enlarged plates obtained under conditions described in our first paper[1] are numbered 1 to 5 for the energetic developer and 6 to 10 for the other developer

Figure 1 shows the position of the enlarged plates on the characteristic curve of the negative material The points *J* and *K* correspond to the speed point according to the Jones criterion[4] (as adopted by the American Standards Association and British Standards Institution) and a point removed from it by one and a half logarithmic units on the exposure axis respectively

The granularity readings were carried out with diaphragms of different dimensions and are characterized by a pair of numbers, the first being the number of the enlarged plate, the second that of the diaphragm[1] For each measurement the instrument was set so as to obtain a sufficiently large reading so that the mean square deviations could be worked out with the same accuracy for all points (*Cf* reference[1] it is sufficient to choose the value of s_0 judiciously)

The mean squares of transparency and density are calculated for each set of granularity readings from the average slope of the probability curve, assuming that the distribution is Gaussian These values are denoted by $\sigma_{G,T}$ and $\sigma_{G,D}$ Then, by graphical integration of the plots of $(\Delta T/T)^2$ against x and $(\Delta D)^2$ against x, we obtain the six

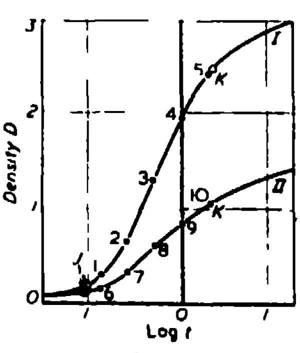

Figure 1 Characteristic curves for the negative emulsion

values of σ_T, σ_{+T}, σ_{-T}, σ_D, σ_{+D} and σ_{-D} In the tables, in which the results of these measurements are assembled, the decimal logarithms of these values are given this has the advantage that the figures in each column have the same absolute accuracy, since the measurements were made with constant relative accuracy

We have also worked out a series of magnitudes which relate the various deviations, as follows

1 Deviations between measurements based on transparency or on density

$$\Delta = \log\sigma_T - \log\sigma_D$$
$$\Delta_+ = \log\sigma_{+T} - \log\sigma_{-D}$$
$$\Delta_- = \log\sigma_{-T} - \log\sigma_{+D}$$
$$\Delta_G = \log\sigma_{G,T} - \log\sigma_{G\,D}$$

2 The same deviations, but worked out theoretically The principle of the method has been described before[2], for our application, Δ_{calc} are calculated from the experimental values of $\log\sigma_T$, the corresponding Δ_{-calc} from $\log\sigma_{-T}$, and Δ_{+calc} from $\log\sigma_{+T}$

3 Differences between experimental and theoretical deviations

$$\delta = \Delta - \Delta_{calc} \qquad \delta_+ = \Delta_+ - \Delta_{+calc}$$
$$\delta_G = \Delta_G - \Delta_{calc} \qquad \delta_- = \Delta_- - \Delta_{-calc}$$

4 Deviations between the same magnitudes, worked out from the probability curve and by graphical integration

$$\delta_T = \log\sigma_{G,T} - \log\sigma_T$$
$$\delta_D = \log\sigma_{G\,D} - \log\sigma_D$$

5 The asymmetry of the probability curves, measured by

$$\Delta_T = \log\sigma_{-T} - \log\sigma_{+T}$$
$$\Delta_D = \log\sigma_{+D} - \log\sigma_{-D}$$

For these values we have calculated the arithmetic means, denoted by a bar, and the quadratic means, shown as $\sigma(\ )$

Experimental data— The experimental data are set out in *Tables I–VI** grouped in three pairs serially In each pair, the first contains all the measured values of granularity, giving positive as well as negative deviations, the second contains all the values for which positive and negative deviations are considered separately and thus characterizes rather better the asymmetry of the distribution curves The first two pairs of tables deal with the same enlarged plates, the only difference is a change in the area investigated and a comparison between the tables will serve to illustrate the reproducibility of the measurements The third pair deals with enlargements which are equivalent to the first, except that the negatives were developed in the fine-grain and not the normal methol-hydroquinone developer

Mean values of the magnitudes set out in the earlier tables will be found in *Table VII* In all tables values representing differences of logarithms are measured in thousandths

Table VII

Quantity	δ_T	δ_D	δ_G	δ	Δ_T	Δ_D	δ_-	δ_+
Arithmetic means	-19_2	-11_0	-0_6	$+0_7$	$+9_0$	$+65_3$	$+2_0$	-1_6
Quadratic means	97_6	24_6	28_7	9_7	—	—	10_6	9_6

Discussion of results— Let us consider first the values of δ_- and δ_+ Their general arithmetic means are very close to zero and one would conclude that the values of Δ_- and Δ_+ are in good agreement with the experiments, since the values of the quadratic means $\sigma(\delta_-) \sim \sigma(\delta_+) \sim 0\ 009_8$ are explained by the experimental errors Regarding $\varepsilon(-)$, the mean square experimental error of a magnitude, the relation

$$\sigma(\delta_\mp) = [\varepsilon^2(\log + \sigma_{\mp T})\varepsilon^2(\log\sigma_{\pm D})]^{\frac{1}{2}}$$

should hold, since

$$\delta_\mp = \log\sigma_{\mp T} - \log\sigma_{\pm D} - \Delta_{\mp calc}$$

The experimental errors of the logarithm of σ_{+T} and $\sigma_{\pm D}$ can be regarded as equal, since the methods used to measure them and their accuracy were the same Introducing

$$\varepsilon(\log\sigma_{\mp T}) = \varepsilon(\log\sigma_{\pm D}) = a$$

we have

$$\sigma(\delta_\mp) = a\sqrt{2}$$

and

$$a = 0\ 006_9$$

which corresponds to relative errors of $\sigma_{\mp T}$ and $\sigma_{\pm D}$ of 1 6 per cent This is of the order that might be expected considering the errors involved in drawing the curves of $(\Delta T/T)^2$ against x and $(\Delta D)^2$ against x and their graphical integration, which was carried out by means of a planimeter Within the accuracy of our measurements, the values of Δ_- and Δ_+ worked out from the theory described earlier are thus in perfect agreement with the measurements

The general arithmetic mean of δ is also negligible, but the spread of the individual values, measured by $\sigma(\delta)$, cannot be explained entirely by experimental errors In fact one can show that if that were the explanation, $\sigma(\delta)$ should be equal to a i e of the order of 6_9 thousandths and not 9_7 We have to admit, therefore, that the calculated values of Δ do not agree with experiment as well as those of Δ_- and

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* We regret that, owing to lack of space, *Tables III* to *VI* have had to be omitted They will be included in the reprints

Table I Granularograms 4—1—2 to 4—4—9 (First series)

Granularogram	$\log\sigma_{UT}$	$\log\sigma_{UD}$	Δ_U	$\log\sigma_T$	$\log\sigma_D$	Δ	δ_T	δ_D	Δ_{calc}	δ_U	δ	$\bar{\delta}_T$	$\bar{\delta}_D$	$\bar{\delta}_U$	$\bar{\delta}$	$\sigma(\delta_T)$	$\sigma(\delta_D)$	$\sigma(\delta_U)$	$\sigma(\delta)$
4—1—2	$\bar{1}$ 023	$\bar{2}$ 636	387	$\bar{1}$ 008	$\bar{2}$ 655	353	+15	−19	[illegible]	+31	− [illegible]								
3	$\bar{2}$ 872	$\bar{2}$ 498	374	$\bar{2}$ 871	$\bar{2}$ 505	366	+1	−7	358$_9$	+15$_1$	+7$_1$								
4	$\bar{2}$ 786	$\bar{2}$ 418	368	$\bar{2}$ 794	$\bar{2}$ 432	362	−8	−14	359$_9$	+8$_1$	+2$_1$								
5	$\bar{2}$ 685	$\bar{2}$ 320	365	$\bar{2}$ 685	$\bar{2}$ 322	363	0	−2	360$_9$	+4$_1$	+2$_1$	−6$_1$	+0$_1$	−8$_2$	−2$_6$	20$_6$	14$_0$	30$_9$	8$_6$
6	$\bar{2}$ 603	$\bar{2}$ 242	361	$\bar{2}$ 585	$\bar{2}$ 215	370	+18	+27	361$_4$	−0$_4$	+8$_6$								
7	$\bar{2}$ 548	$\bar{2}$ 216	332	$\bar{2}$ 554	$\bar{2}$ 207	347	6	+9	361$_4$	−29$_4$	−14$_4$								
8	$\bar{2}$ 376	$\bar{2}$ 055	321	$\bar{2}$ 399	$\bar{2}$ 044	355	−23	+11	361$_6$	−40$_6$	−6$_6$								
9	$\bar{2}$ 161	$\bar{3}$ 857	304	$\bar{2}$ 208	$\bar{3}$ 861	347	−47	−4	362$_0$	−58$_0$	−15$_0$								
4—2—1	$\bar{1}$ 274	$\bar{2}$ 882	392	$\bar{1}$ 254	$\bar{2}$ 901	353	+20	−19	341$_3$	+50$_7$	+11$_7$								
2	$\bar{1}$ 208	$\bar{2}$ 843	360	$\bar{1}$ 214	$\bar{2}$ 863	351	−11	−20	345$_0$	+15$_0$	+6$_0$								
3	$\bar{1}$ 173	$\bar{2}$ 827	346	$\bar{1}$ 192	$\bar{2}$ 825	367	−19	+2	346$_8$	−0$_8$	+20$_2$								
4	$\bar{2}$ 971	$\bar{2}$ 607	364	$\bar{2}$ 992	$\bar{2}$ 629	363	21	−22	356$_3$	+7$_7$	+6$_7$								
5	$\bar{2}$ 940	$\bar{2}$ 579	361	$\bar{2}$ 966	$\bar{2}$ 602	364	−26	−23	357$_0$	+4$_0$	+7$_0$	−13$_0$	−11$_6$	+2$_1$	+3$_0$	18$_9$	18$_9$	24$_7$	10$_8$
6	$\bar{2}$ 856	$\bar{2}$ 515	341	$\bar{2}$ 867	$\bar{2}$ 508	359	−11	+7	359$_0$	−18$_0$	0$_0$								
7	$\bar{2}$ 698	$\bar{2}$ 326	372	$\bar{2}$ 712	$\bar{2}$ 358	354	−14	34	360$_7$	+11$_3$	−6$_7$								
8	$\bar{2}$ 631	$\bar{2}$ 274	357	$\bar{2}$ 649	$\bar{2}$ 286	363	−18	−12	361$_1$	−4$_1$	+1$_9$								
9	$\bar{2}$ 488	$\bar{2}$ 173	315	$\bar{2}$ 505	$\bar{2}$ 158	347	−17	+15	361$_6$	−46$_6$	−14$_6$								
4—3—1	$\bar{1}$ 384	$\bar{1}$ 012	372	$\bar{1}$ 401	$\bar{1}$ 051	350	−17	39	317$_4$	+54$_6$	+32$_6$								
2	$\bar{1}$ 364	$\bar{2}$ 996	368	$\bar{1}$ 392	$\bar{1}$ 039	353	−28	−43	319$_2$	+48$_8$	+33$_8$								
3	$\bar{1}$ 331	$\bar{2}$ 940	391	$\bar{1}$ 341	$\bar{1}$ 016	325	−10	−76	328$_1$	+62$_9$	−3$_1$								
5	$\bar{1}$ 235	$\bar{2}$ 841	394	$\bar{1}$ 220	$\bar{2}$ 870	350	+15	−29	344$_1$	+49$_9$	+5$_9$	−9$_4$	−20$_8$	+21$_8$	+10$_1$	16$_7$	35$_0$	40$_8$	17$_3$
6	$\bar{1}$ 006	$\bar{2}$ 662	344	$\bar{1}$ 016	$\bar{2}$ 654	362	−10	+8	355$_4$	−11$_4$	+6$_6$								
7	$\bar{2}$ 847	$\bar{2}$ 491	356	$\bar{2}$ 858	$\bar{2}$ 504	354	−11	−13	359$_1$	−3$_1$	−5$_1$								
8	$\bar{2}$ 654	$\bar{2}$ 284	370	$\bar{2}$ 647	$\bar{2}$ 286	361	+7	−2	361$_1$	+8$_9$	−0$_1$								
9	$\bar{2}$ 479	$\bar{2}$ 155	324	$\bar{2}$ 500	$\bar{2}$ 127	373	−21	+28	361$_6$	−37$_6$	+11$_4$								
4—4—1	$\bar{1}$ 320	$\bar{1}$ 009	311	$\bar{1}$ 339	$\bar{1}$ 015	324	−19	6	329$_8$	−18$_8$	−5$_8$								
2	$\bar{1}$ 349	$\bar{1}$ 009	340	$\bar{1}$ 362	$\bar{1}$ 016	346	−13	7	325$_4$	+14$_6$	+20$_6$								
3	$\bar{1}$ 302	$\bar{1}$ 009	293	$\bar{1}$ 330	$\bar{2}$ 992	338	−28	+17	330$_6$	−37$_6$	+7$_4$								
4	$\bar{1}$ 123	$\bar{2}$ 767	356	$\bar{1}$ 137	$\bar{2}$ 780	357	14	−13	340$_6$	+15$_4$	+16$_4$								
5	$\bar{1}$ 058	$\bar{2}$ 719	345	$\bar{1}$ 057	$\bar{2}$ 700	357	+1	+13	354$_1$	−9$_1$	+2$_9$	−19$_1$	−2$_4$	−12$_0$	+4$_3$	30$_6$	24$_1$	21$_5$	12$_5$
6	$\bar{2}$ 957	$\bar{2}$ 626	331	$\bar{2}$ 971	$\bar{2}$ 615	356	−14	+11	356$_0$	−25$_0$	−0$_0$								
7	$\bar{2}$ 876	$\bar{2}$ 544	332	$\bar{2}$ 889	$\bar{2}$ 533	356	14	+11	358$_6$	−26$_6$	−2$_6$								
8	$\bar{2}$ 826	$\bar{2}$ 489	337	$\bar{2}$ 854	$\bar{2}$ 493	361	−28	4	359$_3$	−22$_3$	+1$_7$								
9	$\bar{2}$ 480	$\bar{2}$ 117	363	$\bar{2}$ 525	$\bar{2}$ 161	364	−45	−44	361$_5$	+1$_5$	+2$_5$								
									General means			−14$_0$	−8$_7$	+0$_7$	+4$_0$	23$_3$	23$_4$	29$_0$	11

Table II

Granularogram	$\log\sigma_T$	$\log\sigma_{+T}$	Δ_T	$\log\sigma_{+D}$	$\log\sigma_D$	Δ_D	Δ	$\Delta+$	Δ_{calc}	Δ_{+calc}	δ	$\delta+$	$\bar{\Delta}_T$	$\bar{\Delta}_D$	$\bar{\delta}$	$\bar{\delta}+$	$\sigma(\delta)$	$\sigma(\delta+)$
4—1—2	$\bar{2}$ 848	$\bar{2}$ 883	[illegible]	[illegible]	$\bar{2}$ 483	+4[illegible]	[illegible]	400	345$_8$	396$_4$	22$_0$	+3$_6$						
3	$\bar{2}$ 705	$\bar{2}$ 734	−29	$\bar{2}$ 371	$\bar{2}$ 336	+35	334	398	335$_7$	386$_9$	−1$_7$	+11$_1$						
4	$\bar{2}$ 639	$\bar{2}$ 648	−9	$\bar{2}$ 302	$\bar{2}$ 260	+42	337	388	339$_6$	382$_8$	−2$_6$	+5$_2$						
5	$\bar{2}$ 543	$\bar{2}$ 525	+18	$\bar{2}$ 193	$\bar{2}$ 149	+44	350	376	344$_6$	377$_0$	+5$_4$	−1$_0$	+4	+48$_1$	6$_2$	−0$_7$	11$_8$	9$_0$
6	$\bar{2}$ 431	$\bar{2}$ 437	−6	$\bar{2}$ 079	$\bar{2}$ 053	+26	352	384	348$_4$	375$_1$	+3$_6$	+8$_9$						
7	$\bar{2}$ 388	$\bar{2}$ 417	−29	$\bar{2}$ 049	$\bar{2}$ 063	−14	339	354	349$_7$	374$_0$	−10$_7$	−20$_0$						
8	$\bar{2}$ 268	$\bar{2}$ 229	+37	$\bar{3}$ 918	$\bar{3}$ 864	+54	348	365	352$_4$	370$_4$	−4$_4$	−5$_4$						
9	$\bar{2}$ 103	$\bar{2}$ 000	+103	$\bar{3}$ 764	$\bar{3}$ 640	+124	330	360	346$_0$	367$_0$	−16$_0$	−7$_0$						
4—2—1	$\bar{1}$ 089$_5$	$\bar{1}$ 122	−32$_5$	$\bar{2}$ 793	$\bar{2}$ 697	+96	290$_5$	425	280$_0$	418$_3$	+0$_7$	+6$_7$						
2	$\bar{1}$ 046	$\bar{1}$ 079	−33	$\bar{2}$ 719	$\bar{2}$ 667	+52	297	412	297$_6$	413$_0$	−0$_6$	−1$_0$						
3	$\bar{1}$ 032	$\bar{1}$ 050	−18	$\bar{2}$ 713	$\bar{2}$ 628	+85	319	422	300$_0$	410$_9$	+19$_0$	+11$_1$						
4	$\bar{2}$ 805	$\bar{2}$ 872	−67	$\bar{2}$ 468	$\bar{2}$ 490	−22	357	382	347$_9$	395$_6$	+9$_1$	−13$_6$						
5	$\bar{2}$ 829$_5$	$\bar{2}$ 800	+29$_5$	$\bar{2}$ 505	$\bar{2}$ 378	+127	344$_5$	422	345$_6$	390$_9$	−1$_1$	+31$_1$	+4$_1$	+76$_8$	+1$_6$	+4$_6$	7$_6$	13$_8$
6	$\bar{2}$ 737	$\bar{2}$ 695	+42	$\bar{2}$ 398	$\bar{2}$ 307	+91	339	388	333$_4$	385$_0$	+5$_6$	+3$_0$						
7	$\bar{2}$ 577	$\bar{2}$ 543	+34	$\bar{2}$ 235	$\bar{2}$ 173	+62	342	370	342$_0$	378$_6$	0$_0$	−8$_6$						
8	$\bar{2}$ 513	$\bar{2}$ 484	+91	$\bar{2}$ 167	$\bar{2}$ 093	+74	346	389	345$_6$	376$_4$	+0$_4$	+12$_6$						
9	$\bar{2}$ 381	$\bar{2}$ 324	+57	$\bar{2}$ 049	$\bar{3}$ 955	+94	332	369	349$_0$	372$_0$	−17$_0$	−3$_0$						
4—3—1	$\bar{1}$ 233	$\bar{1}$ 266	−33	$\bar{2}$ 955	$\bar{2}$ 829	+126	278	437	249$_4$	435$_8$	+28$_6$	+1$_2$						
2	$\bar{1}$ 216	$\bar{1}$ 264	−48	$\bar{2}$ 931	$\bar{2}$ 836	+95	285	428	255$_1$	434$_0$	+29$_9$	−6$_0$						
3	$\bar{1}$ 182	$\bar{1}$ 198	−16	$\bar{2}$ 928	$\bar{2}$ 777	+151	254	421	265$_2$	426$_0$	−11$_2$	−5$_0$						
5	$\bar{1}$ 055	$\bar{1}$ 083$_8$	−28$_8$	$\bar{2}$ 748	$\bar{2}$ 688	+60	307	395$_5$	295$_7$	414$_4$	+11$_3$	−18$_9$	−15$_2$	+73$_9$	+6$_2$	+1$_6$	15$_8$	12$_8$
6	$\bar{2}$ 865	$\bar{2}$ 866	−1	$\bar{2}$ 542	$\bar{2}$ 459	+83	323	407	322$_3$	395$_8$	+0$_7$	+11$_2$						
7	$\bar{2}$ 714	$\bar{2}$ 700	+14	$\bar{2}$ 384	$\bar{2}$ 318	+66	330	382	335$_1$	385$_0$	−5$_1$	−3$_0$						
8	$\bar{2}$ 506	$\bar{2}$ 487	+19	$\bar{2}$ 161	$\bar{2}$ 100	+61	345	387	345$_0$	377$_9$	0$_0$	+9$_1$						
9	$\bar{2}$ 394	$\bar{2}$ 369	−29	$\bar{3}$ 986	$\bar{3}$ 967	+19	348	396	351$_8$	373$_4$	−3$_8$	+22$_6$						
4—4—1	$\bar{1}$ 193	$\bar{1}$ 180	+13	$\bar{2}$ 933	$\bar{2}$ 761	+172	262	410	261$_8$	424$_0$	+0$_1$	−5$_0$						
2	$\bar{1}$ 198	$\bar{1}$ 224	−26	$\bar{2}$ 916	$\bar{2}$ 799	+117	282	425	260$_9$	429$_0$	+21$_1$	−4$_0$						
3	$\bar{1}$ 180	$\bar{1}$ 179	+1	$\bar{2}$ 907	$\bar{2}$ 748	+159	273	431	296$_4$	444$_8$	−23$_4$	+6$_2$						
4	$\bar{2}$ 982	$\bar{2}$ 991	−9	$\bar{2}$ 651	$\bar{2}$ 605	+46	331	386	308$_0$	405$_0$	+23$_0$	−19$_0$						
5	$\bar{2}$ 914	$\bar{2}$ 899	+15	$\bar{2}$ 585	$\bar{2}$ 507	+78	329	392	316$_3$	397$_0$	+12$_7$	−5$_0$	−0$_2$	+83$_2$	+6$_7$	−5$_4$	14$_4$	8$_2$
6	$\bar{2}$ 822	$\bar{2}$ 819	+3	$\bar{2}$ 492	$\bar{2}$ 431	+61	330	388	326$_3$	392$_1$	+3$_7$	−4$_1$						
7	$\bar{2}$ 761	$\bar{2}$ 713	+48	$\bar{2}$ 422	$\bar{2}$ 334	+88	339	379	331$_6$	385$_8$	+7$_4$	−6$_8$						
8	$\bar{2}$ 701	$\bar{2}$ 706	−5	$\bar{2}$ 346	$\bar{2}$ 393	+90	345	380	336$_0$	385$_6$	+9$_0$	−5$_6$						
9	$\bar{2}$ 350	$\bar{2}$ 306	44	$\bar{3}$ 995	$\bar{2}$ 026	31	337	370	330$_7$	374$_0$	+6$_3$	−4$_0$						
										General means			−1$_8$	+70$_8$	+2$_1$	−0$_3$	12$_8$	11$_6$

Δ_+ but that they contain a systematic error of the order of

$$s(\Delta_{calc}) = [(9_7)^2 - (6_9)^2]^{1/2} \sim 6_8 \text{ thousandths}$$

which corresponds to 1 6 per cent in antilogarithms The reason for this error, which does not occur for $\Delta_{\mp calc}$ may be found in the fact that in calculating Δ_{calc} the asymmetry of the probability curve giving the deviations of transparencies from their mean is completely neglected If this is taken into account, a more correct value Δ^*_{calc} can be worked out from $\log \sigma_{-T}$, $\log \sigma_{+T}$, Δ_- and Δ_+ *Table VIII* gives some more accurate figures

Table VIII

Source	Grain histogram	Δ	Δ_{calc}	Δ^*_{calc}	δ	$\delta^* = \Delta - \Delta^*_{calc}$
Table I	3—1	350	317_4	330_1	$+32_6$	$+19_9$
	3—2	353	319_8	336_6	$+33_2$	$+16_4$
Table III	4—1	331	351_6	346_4	-20_6	-15_4
	5—1	362	340_1	361_9	$+21_9$	$+0_8$

The general arithmetic means of δ_T and δ_D differ from zero This indicates certain systematic deviations—not large—between the two methods of measuring the mean square fluctuations *i e* using the probability curve or the graphical integration of the curves of $(\Delta T/T)$ against x, and $(\Delta D)^2$ against x Since the values of the two means are very nearly the same, this systematic difference characterizes the difference of the methods regardless of the values of $(\Delta T/T)$ or (ΔD) with which they are concerned If one converts the differences into relative errors, their values come to about 3 per cent

The scatter of the individual readings around their mean may be estimated by

$$\sigma'(\delta_z) = [\sigma^2(\delta_z) - \delta_z^2]^{1/2} \sim 22_6 \text{ thousandths}$$

z being equal to T or D Since

$$\delta_z = \log \sigma_{G_z} - \log \sigma$$

this scatter can be explained as experimental error if $s(\log \sigma_{G_z}) = \gamma = [\sigma'^2(\delta_z) - \alpha^2]^{1/2} = 22_1$ thousandths *i e* if the errors of the measurements taken off the probability curve are of the order of 5 per cent This is acceptable having regard to the difficulty of drawing a straight line through a set of experimental points, the nearer these lie to a straight line the smaller become the deviations between the two methods of measurement

Regarding the systematic deviations described above, yet another difficulty may be made responsible Different persons will assign different weights to points according as they are situated near the centre or near the end of the curve in this way it is possible to obtain either positive or negative values of δ_T and δ_D

Examination of the distribution of the values of σ_G confirms the preceding deductions In fact the errors of Δ_{calc} are negligible compared with those of $\log \sigma_{G\,T}$ and $\log \sigma_{G\,D}$ Since

$$\delta_G = \Delta_G - \Delta_{calc} = \log \sigma_{G\,T} - \log \sigma_{G\,D} - \Delta_{calc}$$

we get

$$\delta_G = 0 \quad \text{and} \quad \sigma(\delta_G) \sim \gamma\sqrt{2} \sim 31 \text{ thousandths}$$

which is in good agreement with the experimental figures

Finally we must consider the means of Δ_T and Δ_G in *Table VII* The first are always much smaller than the second One would conclude that the distribution of fluctuations in transparency is, on the whole, much more symmetrical than that of density This finding to some extent justifies the basis which has been used for deriving[2] the theoretical values of Δ, Δ_- and Δ_+, since the transparency fluctuations are practically Gaussian

The variations of σ_T and σ_D with the size of the diaphragm are extremely irregular The values decrease as the aperture grows, but always at a rate much below that to be expected from SELWYN'S theory[5] On changing from diaphragm No 1 to No 9, the $\log \sigma_T$ or $\log \sigma_D$ should vary by as much as 1 3, a value we have never obtained, on average the value of the variation is no more than 0 6

Comparison of *Tables I* to *IV* shows clearly the lack of *reproducibility of the measurement of granularity* at different spots on the same enlargement This is not due to the experimental methods but to the extreme irregularity of the quantity under investigation

Conclusions— The following conclusions may be drawn from the preceding discussion, remembering that it may be necessary to repeat the work on other emulsions

1 The granularity of enlarged images cannot be defined accurately by the examination of either density or transparency fluctuations near a single point on the negative One cannot hope to obtain a satisfactory result unless one examines a large number of points chosen at random from the area of the negative

2 The granularity of enlarged images may be measured equally well by determining deviations of the transparency or of the density Measurements of one sort can be converted into measurements of the other Accuracy will be the same if the lack of symmetry of the distribution curve observed can be assessed, if not, a supplementary error of the order of 1 6 per cent is to be expected

3 Probability curves should not be used if an accuracy better than 5 per cent is needed and the curves are somewhat wavy like those we have often observed

4 The change in the mean square deviations of transparency or of density as a function of the size of the scanning spot is less than that to be expected from the Selwyn theory

CONSTRUCTION OF A NEW GRANULARITY METER

Introduction— The need for measuring the granularity at a large number of points on an enlarged negative requires an instrument and methods which are much more rapid than those in use so far A design has been evolved to meet this need and a successful instrument has been constructed in this way The instrument has been so designed as to enable the granularity to be measured on an original negative or on an enlargement it is universal

Principle of apparatus—The granular negative is supported by a sunk rotating table which can be displaced by means of a micrometer screw The distance between the axis of rotation and the optical axis of the ray of light feeding the scanning spot can thus be adjusted within 0 01 mm from 0 to 15 mm A microscope lens forms on the negative a circular luminous spot, the size of which is governed by the size of the diaphragm of which the spot is the image, and by the degree of enlargement This diameter can be varied between 3 5 μ and 3 mm The luminous intensity can be changed by means of a sensitometric step tablet and neutral grey filters The lamp has a concentrated filament (8 v, 6 a, Philips 6019M) and is fed from the mains supply (110 v, DC) buffered by an accumulator battery The current is adjusted by a circuit resembling a Wheatstone bridge, one of the arms of which contains the lamp and is constant to less than 1 part in 10^3

The first photoelectric cell, of the electron multiplier type, receives the light passing through the granular negative , a second similar cell is illuminated directly from the lamp, the intensity being adjusted to any desired value by means of a set of neutral filters and a sensitometric step tablet

The photoelectric currents produced by the two cells are converted into potential differences by means of two fixed resistances These potentials are applied to a pair of triodes connected in opposition The amplifier will deliver no current if the currents from the photoelectric cells passing along the series resistances are, on the average, balanced So as to be able to vary the illumination to cause the amplified current to become zero, the current is measured by means of a null galvanometer As one of the photoelectric currents varies rapidly, following the fluctuations of the transparency of the granular plate, an amplified AC current is produced This AC current has no well defined frequency and will represent exactly the fluctuations in transparency, provided that the amplifier is exactly linear and the photoelectric current strictly proportional to the intensity of the light These conditions are fulfilled in the apparatus we have constructed

The amplified AC current is received by a thermocouple , this will deliver a current which is proportional to the mean square of the varying current, whatever its frequency This method thus measures $\sigma^2(\Delta i)$ where Δi represents the amplified currents produced by the differences in illumination received by the two cells We have thus a relative measure of $\sigma^2(\Delta T)$ since the currents are proportional to the luminous flux

In order to obtain absolute measurements one would proceed as follows

1 The electronic system is first balanced without any light falling on to the cells

2 One of the cells is illuminated and balance is re-established by varying by an amount V_0, the grid potential of the triode affected by means of an auxiliary potentiometer circuit

3 A similar voltage change V_0 is applied to the grid of the second triode and the circuit is balanced once more by illuminating the second cell The amplifier then works under the same conditions as at *1*

4 If now the potential V_0 applied to the first cell by means of the potentiometer circuit is varied within $\pm\ \Delta V$, the deflection l of the galvanometer measuring the output from the thermocouple is

$$l = k(\Delta V)$$

where k is a proportionality factor which depends uniquely on the amplifier and the characteristics of the thermocouple and the galvanometer This coefficient can therefore be determined

5 The granular negative is then inserted in the path of the light illuminating the first cell and rotated, and the light intensity is varied until the amplified current is zero The AC current is then measured by means of a deflection l' which can be converted, since k is known, into a value of $\Delta V'$ which represents the mean square of the potential variations on the grid, caused in turn by the fluctuations in light intensity

Under these conditions, V'_0 is proportional to the average illumination $\bar{E}$ on the cell, and $\Delta V'$ to the mean square of the fluctuation $\sigma(\Delta E)$, $\Delta V'/V_0$ is consequently a measure of the mean square of the variation in relative transparency of the granular layer

$$\frac{\Delta V'}{V_0} = \frac{\sigma(\Delta E)}{E} = \frac{\sigma(\Delta T)}{T} = \sigma_T$$

Some details of the apparatus—*Figure 2* shows the arrangement of the optical system while *Figure 3* gives the schematic layout of the electronic part of the apparatus which is an entirely original feature

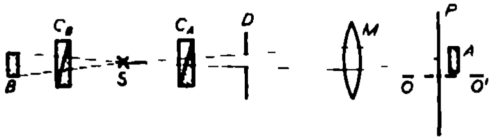

Figure 2 Optical part of granularity meter S source of light, C_A and C_B neutral step wedges and filters, D diaphragm M microscope objective, P granular layer rotating around O—O', A and B photoelectric electron multiplier cells

The photo-emitting cathodes of the multiplier cells (RCA 931A) are held at − 1,000 v and the subsequent electrodes are held at potentials progressing in steps of 100 v up to the final anodes These latter are connected through series resistances R_A and R_B into the sliders of a potentiometer X Y so that the potential can be varied in the region of the normal grid potential of the amplifier triodes These are of the type 6J6 in fact double triodes are used, the corresponding parts being connected in parallel so that the slope of the characteristic is doubled (In *Figure 3* these details are not shown) The 6J6 valves are supplied at 220 v and their anode resistances are 10^4 ohms approximately, chosen so as to produce linear amplification within the range to be used One of these resistances is variable to enable the tubes to be balanced $G_=$ indicates the null galvanometer and $G_\sim$ indicates the thermocouple-galvanometer assembly

The potentiometer operates in steps, four values of potential V_0 can be set, corresponding to resistance values 0, 40, 100 and 250 ohms, separately for both cells Furthermore, for the cell which is illuminated through the granular negative, steps of ± 5, ± 10, ± 15 and ± 20 ohms are available In this way the scale of the thermocouple-galvanometer can be accurately calibrated Since the variations are quadratic, the scale is calibrated according to a square law

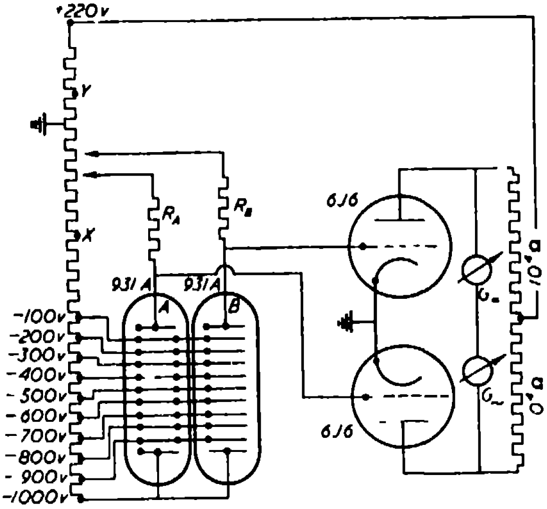

Figure 3 Schematic diagram of electronic part of granularity meter

The power supply for the cells and the amplifier is connected to the main AC supply through a transformer, rectifier and smoothing circuits and electronic stabilization of the potentials

The measurable values of σ_T cover a range from 0·5 to about 0·01, the accuracy has not yet been determined but is certainly better than 5 per cent

ACKNOWLEDGEMENTS

The foregoing paper reports development of the technique previously described[1] *The author wishes to thank Professor A Hautot, director of the laboratory, l'Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture (I R S I A) and S A Photoproduits Gevaert for their financial support, and M Liebens, radio engineer, who assembled the electronic part of the granularity meter Acknowledgement is also due to Dr W F Berg for translating this paper from the French*

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Effect of Molecular Size on Sorption Hysteresis

Of the many explanations of sorption hysteresis which have been advanced, only the 'open pore' theory makes any quantitative predictions According to this theory[1], hysteresis arises from delay in formation of the meniscus at the stage where layer adsorption gives way to capillary condensation and it is evident that the larger the diameter of the adsorbed molecules and the thicker the adsorbed layer, the more easily will an open pore of given diameter become blocked at its narrowest point This explains why, on many adsorbents, only water shows a hysteresis loop A detailed examination of the sorption of aliphatic alcohols from methyl to *n*-butyl by silica gel[2] showed no appreciable change in the size of the loop, although water with a smaller molecule showed a much larger loop Extension of this work to substances of still larger molecular diameter was interrupted by the war, but it had already been found[3] that triethylamine, on the same adsorbent, gave an exceedingly small loop, which was difficult to locate exactly Work has now been resumed on a similar gel, which also gives a large loop with water and a small loop with the ethyl alcohol, and a systematic examination of the sorption isothermals of the primary aliphatic amines is now in progress We have found that the hysteresis loop persists as far as *n*-propylamine but is absent with the higher homologues, *i* butyl-, *n*-amyl-, *n*-hexyl- and *n*-heptyl amines The most important prediction of the open pore theory has thus been confirmed

If sorption hysteresis were due to hysteresis of the contact angle as originally suggested by Zsigmondy[4], or to hysteresis in two dimensional phase changes in the adsorbed layer[5], as is sometimes found in trough films, there would be no reason to expect that the molecular diameter would determine the size of the loop

A rival theory which has attracted some attention in recent years is the so-called 'ink bottle' theory, due originally to Kraemer[6] but later elaborated by Rao[7] and, more recently, by Katz[8] According to this view, the majority of the pores of the adsorbent have bottlenecks, being narrower at their open ends than in the middle The advocates of this theory claim that the adsorption curve represents the true equilibrium state[7] and that certain quantitative relations hold between the pressures at corresponding points on the two branches of the loop[9] The first claim is contrary to all available experimental evidence, which shows quite clearly that only the desorption curves are consistent with the Kelvin equation[1, 10], the second is based on an incorrect application to a cylindrical meniscus of the Kelvin equation, the correct form[11] of which was given by one of us in 1936 The effect of increasing molecular diameter on adsorption in 'ink bottle' capillaries would not be apparent until the molecule becomes too large to enter the bottleneck Then there would be no hysteresis and no adsorption Now it has been shown by Broad and Foster[1] that the 'persorption' effect observed with some types of silica gel can be explained by assuming that these gels contain tapering capillaries which are open at their wider ends The extent to which a molecule can penetrate such a pore depends on the molecular diameter but the adsorption does not fall to zero until the molecular diameter exceeds that of the wide open neck of the pore If bottlenecks were present in these gels any molecule smaller in diameter than the neck of the pore would be able to enter, whereas all molecules with diameters greater than that of the neck would be excluded *i e* there should be an abrupt deviation from Gurvitsch's rule at a certain critical diameter But, in fact, there is a gradual decrease in the volume adsorbed as the diameter increases It may therefore be concluded that this particular type of gel has no 'ink bottle' pores, yet a large hysteresis loop is observed with water Another argument against the 'ink bottle' theory has been advanced by Barkas[13] who maintains that the liquid inside the 'ink bottle' is unstable when put in tension by the meniscus in the narrow neck It appears to us, therefore, that the balance of evidence is now in favour of the open pore theory Further work on the factors determining the size of the hysteresis loop is in progress

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Formation of 'Hair Line Cracks' by Hydrogen introduced into Steel by Electrolysis

It has been established that in many steels hair line cracks (' flakes ') can be produced in the laboratory by soaking specimens in hydrogen at high temperatures, quenching and aging[1,2] When nitrogen is used in an otherwise similar treatment hair line cracks do not develop

An alternative method of introducing hydrogen into a specimen is to make it the cathode in the electrolysis of dilute mineral acid, and it has been shown that hair line cracks may be formed when hydrogen is introduced into steel in this way

In one typical experiment a steel of the following composition was used

Carbon	0 28 per cent
Manganese	0 26 per cent
Nickel	3 19 per cent
Chromium	1 35 per cent
Molybdenum	0 31 per cent

A bar 4 cm diam was soaked at 1,300°C and oil quenched, tempered just below its Ac_1 point (710°C), heated to and water quenched from 1,000°C and finally tempered at 300°C The specimen was then cut into two equal cylinders of which one was mounted as the cathode in a bath of 1 per cent sulphuric acid and a current of about 0 005 amp/sq cm was passed for ten days The other cylinder was given no further treatment

Thin disks were cut from each cylinder and were deeply etched in boiling hydrochloric acid radial cracks 1 to 3 mm long were revealed near the circumference of the specimen treated in the electrolytic bath but not in the control specimen Other similar disks were quenched and fractured along their diameters when small typical ' flakes ' were found near the surface in the treated specimen only see *Figure 1*

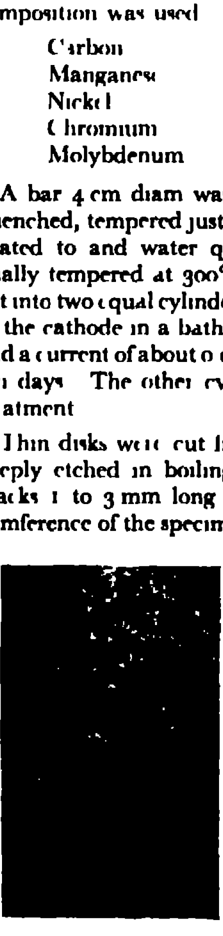

Figure 1 A ' flake ' (hair line crack) in the fracture of a steel into which hydrogen had been introduced by electrolysis Approximate magnification × *8*

This experiment, which is in accord with the simple hydrogen pressure theory[3], shows that the quenching of an actual solution of hydrogen in steel need not be involved in any explanation of hair line crack formation It also suggests that thermal or transformation strains due to the quenching play only a secondary part in the process

These experiments were carried out early in 1941 in the Department of Metallurgy of the University of Sheffield, and the author wishes to acknowledge the interest and help then received from Professor J H Andrew

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Separation of Small Spheres According to Size

We have developed the technique of making small spheres previously described by Sollner[1], and we have sorted them according to size by a method which we have not seen mentioned before

The spheres are made by mixing ground glass particles into the air supply of a gas blowpipe , only those traversing the hotter regions of the flame are collected Overheating produces spheres with included bubbles, while underheating results in many particles of irregular shape We have not been able to avoid both these difficulties simultaneously with soda glass, but have obtained good results with Chance's *Hysil*

We have not found the standard method of sedimentation with decantation satisfactory for separating the spheres into narrow size ranges, and we have had little success with other methods such as shaking the particles through a slit We have therefore considered a simple sedimentation method in which all the spheres are released simultaneously at the top of a static fluid column, and are collected in timed fractions at the bottom In practice, however, such a column, when composed of a single liquid, is unstable the layer containing the spheres has a greater mean density than the layer immediately below, so a convection takes place in which liquid containing spheres of all sizes swirls downwards, while clear liquid from below moves upwards to take its place The speed of convection is far greater than that of fall under Stokes' law, both small and large spheres being carried down at the same rate , this completely spoils the separation We are indebted to Dr **Frank** for the suggestion, also made by **Clerk Maxwell**, that instability of this type could be avoided if the density of the static column were made to increase from top to bottom. We find that this is borne out in practice, and we now use alcohol/water columns graded in density from 0·87 gm/cc at the top to 1·0 gm/cc at the base.

A column height of 20 cm is sufficient to give the degree of separation quoted below for particles 10 μ in diameter. Longer columns are required for larger particles, giving in all instances about the same time of separation, which is roughly 3 hr. Longer columns should give a higher degree of separation at the expense of time. Columns with circular cross sections up to 15 cm in diameter have been used.

Spheres with diameters ranging from 5 to 40μ have been separated in one operation giving over 90 per cent of all those in one dish within ± 5 per cent of the mean size. There are few particles that are seriously unspherical; measurements on the worst shaped member of a sample of twenty particles gave a maximum to minimum diameter ratio of 1·02. The amount of material separated in each operation is at present small, amounting to only 0·3 gm, but it is possible to make at least 3 runs in the same column without destroying the density gradient.

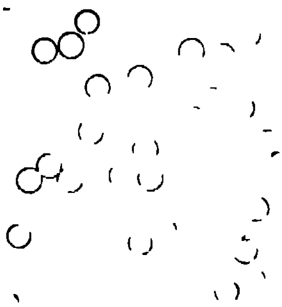

Figure 1 Photomicrograph of Hysil glass spheres, mean diameter 14μ, immersed in water

The method of separation might be applied directly to the size distribution analysis of powders, and particularly to a method depending on the scattering or absorption of light by the particles as they cross a given horizontal section. The spheres produced by the foregoing technique should be useful for any application requiring standard particles with diameters between 1 and 100 μ. They might if necessary be coated with metal by vacuum evaporation.

The photomicrograph, *Figure 1*, shows the degree of uniformity achieved.

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One dimensional Flow behind a Steady Plane Detonation

According to the accepted theory of plane detonation the equilibrium reaction products have a well defined initial forward velocity W_1 which together with their acoustic velocity a_1 and the velocity D of the wave itself satisfy the Chapman-Jouguet (CJ) relation

$$W_1 + a_1 = D \tag{1}$$

Considerations of momentum show[1] that the products must subsequently decelerate. The steady reaction zone is therefore followed by a rarefaction which will become less steep with time. The structure of this rarefaction has been analysed by **Taylor**[2] and **Penney**[3]. If detonation is initiated at $x = 0$, $t = 0$, and moves with constant velocity D the flow is defined by

$$x = (W + a)t \tag{2}$$

$$\text{where} \qquad W_1 - W = \int_{\varrho}^{\varrho_1} a \, d\varrho/\varrho \tag{3}$$

and ϱ is the density corresponding to W. Equation 3 is to be supplemented by the adiabatic relation. In particular, if this has the form

$$p = \text{constant} \times \varrho^{\gamma} \tag{4}$$

equation 2 becomes

$$\frac{W}{W_1} = 1 - \frac{2D}{(\gamma + 1) W_1}\left(1 - \frac{x}{Dt}\right) \tag{5}$$

In the present note we are concerned with the motion of a typical material element, in other words with the 'Lagrangian' solution. This is defined by

$$\frac{dW}{dt} = \frac{\partial W}{\partial t} + W \frac{\partial W}{\partial x} \tag{6}$$

which by equation 5 reduces to

$$t\frac{dW}{dt} = \frac{\gamma - 1}{\gamma + 1}(W_1 - W) - \frac{2a_1}{\gamma + 1} \tag{7}$$

Integration of equation 7 gives

$$\frac{dx}{dt} = W = W_1 - \frac{2a_1}{\gamma - 1}\left[1 - \left(\frac{t_0}{t}\right)^{\frac{\gamma - 1}{\gamma + 1}}\right] \tag{8}$$

where t_0 is the instant at which the chosen element traverses the CJ plane. A second integration yields

$$\frac{x}{Dt_0} = \left(1 - \frac{\gamma - 1}{\gamma + 1}\frac{a_1}{D}\right)\frac{t}{t_0} + \frac{\gamma + 1}{\gamma - 1}\frac{a_1}{D}\left(\frac{t}{t_0}\right)^{2/(\gamma + 1)} \tag{9}$$

which is the required particle path. According to equations 8 and 9, the particle decelerates and reverses its direction of motion at (x', t') where

$$\frac{t'}{t_0} = \left(1 - \frac{\gamma - 1}{2}\frac{W_1}{a_1}\right)^{\frac{(\gamma + 1)}{\gamma - 1}} \tag{10}$$

$$\frac{x'}{Dt_0} = \frac{a_1}{D}\left(1 - \frac{\gamma - 1}{2}\frac{W_1}{a_1}\right)^{-2/(\gamma - 1)} \tag{11}$$

The locus of turning-points in the (x, t) plane is thus a straight line

$$\frac{x'}{Dt'} = 1 - \frac{\gamma + 1}{2D} W_1 \tag{12}$$

as is otherwise obvious from equation 5

If we use the well known approximations

$$W_1 \approx \frac{D}{\gamma + 1} \approx \frac{a_1}{\gamma} \tag{13}$$

and write $\nu = (\gamma - 1)/(\gamma + 1)$, these results become

$$\nu \frac{W}{W_1} = (1 + \nu)\left(\frac{t}{t_0}\right)^{-\nu} - 1 \tag{14}$$

$$2\nu \frac{x}{Dt_0} = (1 + \nu)\left(\frac{t}{t_0}\right)^{1-\nu} - (1 - \nu)\frac{t}{t_0} \tag{15}$$

$$\frac{2x'}{Dt_0} = \frac{t'}{t_0} = (1 + \nu)^{1/\nu} \tag{16}$$

which in turn for almost isothermal conditions $(\nu \sim 0)$ approach

$$\frac{W}{W_1} = 1 - \ln\frac{t}{t_0} \tag{17}$$

$$\frac{2x}{Dt_0} = \frac{t}{t_0}\left(2 - \ln\frac{t}{t_0}\right) \tag{18}$$

$$\frac{2x'}{Dt_0} = \frac{t'}{t_0} = e = 2.718 \tag{19}$$

If motion is prevented at $x = 0$, for example by enclosing the explosive in a tube rigidly sealed at the plane of initiation, the particle remains at rest after reaching x'. If the tube is open, equations 8 and 9 continue to apply while the particle returns through its initial position Dt_0 and ultimately passes out at the open end.

Wave speed photographs of detonating gases frequently contain, in addition to the straight edge which indicates the steady velocity of the wave front, a family of curved lines corresponding to much lower velocities and generally taken to define the movement of the luminous products[4]. An unusually fine example, due to BONE and FRASER[5], is reproduced in *Figure 1a*. The locus of turning-points on the curved paths is, in fact, a straight line of which the slope is one half that of the wave trace as predicted by equation 16. The comparison can, however, be carried further by using equation 15 and assigning a value to γ. *Figure 1b* was drawn in this way with $\gamma = 1.2$ (a probable value). The theory is well confirmed, since the two figures may be almost exactly superimposed.

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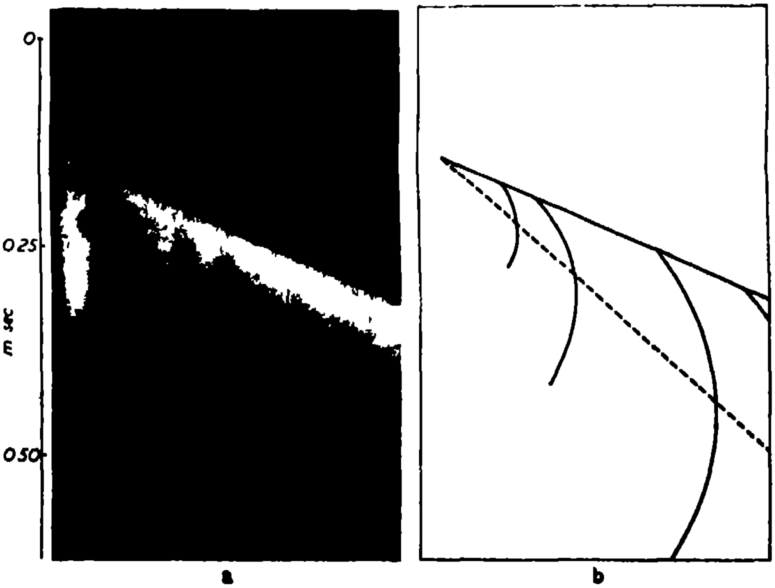

Figure 1 *Flow behind a steady plane detonation in a gaseous explosive* a *Moving-film photograph by* BONE *and* FRASER[5] *of initiation of detonation in* $C_2H_2 + O_2$ (*By permission of Royal Society*) b *Theoretical trace, according to equation 15 with* $\nu = 1/11$ *when* $\gamma = 1.2$

Commentary: Science—its Sphere of Influence

THIS SUBJECT may seem vague and meaningless, even to many scientists. To those, however, who have spent many years in research and teaching there come disquieting moments of retrospection. New discoveries of varying degrees of importance have been made, new techniques have been devised, new applications have been made of facts and principles, and the record of science and scientists looks good. Yet there often comes the melancholy reflection that the greatest progress may have been in the applications of science to material things and in the intellectual development of scientists themselves rather than in the enlightenment of people in general

Science still has a too narrowly restricted significance to too many people, including many students who have been exposed to courses in various fields of science The reasons given to the writer by a random sample of intelligent people for their appreciation of science included more durable paint on automobiles, improved milking machines, faster aeroplanes, firmer ice cream, better varieties of wheat, better toothpaste, ball point fountain pens; electric razors, and nylon stockings At least science and technology had made some impression on each of the individuals who prided themselves on knowing something about 'the wonders of science'. It must be conceded that many better examples were cited, but almost all indicated that the concept of the value of science was limited to those things that increase personal comfort and convenience The writer would be the last to disparage the services rendered by applied science and technology as he himself is in a field of applied science, but has science rendered its full measure of service when it concentrates too much on increasing the comforts of civilization? Is it contributing as much as possible to the progress of civilization in the deepest and fullest sense? Is there danger that science itself may sometimes become too authoritarian in its attitude and too limited in its interests? Is there sometimes a tendency to concentrate too exclusively on the facts of science and to neglect its significance in the development of the scientific attitude towards problems of living? Possibly it is the neglect or perversion of the spirit of science that has provoked criticism of science and of the scientific attitude. However that may be, the widespread criticism of science and scientists has provoked the writing of this Commentary

In the long and complex process of man's evolution towards intellectual enlightenment and spiritual refinement there have often been misgivings that intellectual development was progressing faster than ethical development. Even today fears are expressed that our civilization is menaced, that science is largely to blame, and that there should be a moratorium on science until man's spirit can overtake his intellect and guide it aright.

Science is charged implicitly or explicitly with dealing in black magic, with being dehumanizing rather than humanizing, and with putting new tools into man's hands without at the same time guaranteeing that he will use them properly.

Through the ages men have been both fascinated and frightened by science, especially those who knew little about it and found its discoveries disruptive of the *status quo* Consequently scientists have paid heavy penalties for their discoveries and teachings For almost two thousand years philosophers and scientists who tried to substitute truth for dogma either did so cautiously or paid for their incaution. They were considered deluded, dangerous, in league with the devil The Faust legend of the Middle Ages is eloquent of the superstitious awe and fear of men who had delved into Nature's secrets enough to confuse the uninitiated or disturb their intellectual orthodoxy Scientists in most of the modern world do not risk life or liberty even if they substitute new truths for old errors, in the natural sciences at least they are relatively immune from anything more serious than the frowns of society Is this completely true in the field of the social sciences, are penalties ever imposed on the unorthodox? Have we emancipated ourselves completely from the tyranny of our presuppositions and prejudices? How enlightened are we when we are still afraid that the truth may be unpleasant and upsetting? Does a faint taint of suspicion of black magic still cling to certain spheres of science?

SCIENCE AND THE HIGHER FACULTIES

The charge is often preferred that science substitutes cold reason for the higher faculties, that it concentrates on the material and neglects the spiritual, that it stifles the imagination and the finer feelings, that it tends to suppress the aesthetic and the ethical 'We have developed a marvellous material civilization before we were spiritually ready for it' is a thesis often stated and elaborated, possibly with some justification. Is science to blame if spiritual development has actually lagged behind intellectual development?

Is it true that science and technology stifle the imagination and blunt the finer faculties? Certainly a good scientist must have the kind of creative imagination that enables him to formulate scientific hypotheses and discover truths What can stimulate the imagination more than study of the infinite vastness of the universe, what can stimulate the imagination more than study of the vast potentialities of a single-celled micro-organism, what can stimulate the imagination more than the evolution of plants and animals, and what can stimulate the imagination more than the development of man himself from such small beginnings?

Poets, peasants and scientists can all see and feel the beauty of a sunset, but many equally inspiring phenomena are hidden to all but those who master the technique for observing them The sense of beauty in the perfection of natural phenomena need not be sullied because of attempts to understand them.

Final explanations of many phenomena have hitherto eluded man's intelligence and inventiveness, possibly they always will, possibly man is incapable of really explaining himself to himself The scientist wonders and thinks, and continues his quest for facts and explanations, he is dull indeed if his imagination does not carry him beyond the limits of his knowledge and if the insignificance of his knowledge does not teach him the lesson of humility Like everyone else scientists may have their fancies, but, as scientists, they must distinguish between facts and fancies They may have their ideals, but, as scientists, they must distinguish between ideals and realities

The complaint is often made that science tends to harden and coarsen the spirit rather than to soften and refine it Science seeks after truth about the universe in which we live; it seeks facts and natural laws, it attempts to utilize those facts and laws to emancipate man from ignorance and fear of the unknown, from the tyranny of his environment, from the limitations of his own physical powers, and from the tyranny of his own baser passions Can those objectives be dehumanizing? Science and technology have made it possible for man to free himself from many fears and limitations. They have shown man how more easily to feed, clothe and shelter himself, to retain his physical and mental health, to make machines do what he himself cannot do. Is it dehumanizing to enable man to live longer and more comfortably, even though comfort is not all of civilization? Can it be dehumanizing for man to study himself and his relations to himself? Is anything really more humanizing than man's attempt, through the natural and social sciences, to study himself, his powers, his imperfections, his evolution towards intellectual enlightenment and spiritual refinement?

Just as the natural sciences strive to understand the physical man and his physical environment, so do the social sciences strive to understand factors affecting social behaviour, just as the natural sciences try to enable man to utilize facts and principles to his own advantage, so do the social sciences try to give man facts and principles that should enable him to live more happily with himself and his fellow human beings Unhappily, man does not utilize the facts and principles of the social sciences to the same degree as those of the natural sciences, because in his relationship with himself man's passions often suppress his reason and he becomes cruel to himself Are the social sciences to blame for man's inhumanity to man? To humanize himself man needs more science not less, even though he may need more than science religion, poetry, music, art—each according to needs and values

RESPONSIBILITIES OF THE SCIENTIST

It is true that science often gives man new tools without guaranteeing that he will use them to his own advantage Society often has demanded those very tools and then has criticized scientists for having satisfied the demand As an example, during the 1914–18 war the slogan was 'Food will win the war', and farmers and agricultural scientists were importuned to do everything possible to increase production As patriotic citizens they did their best, and the best was good Then came the agricultural depression, followed by a general depression, during which popular pundits declared that scientists had been guilty of promoting over-production The doctrine was preached that the world was producing so much more than it could consume that production must be restricted, even when there was hunger in many lands. In the U S A. measures were taken to restrict production to effective market demand. Then came drought years, outbreaks of insect pests and of plant diseases; and the doctrine of the ever-normal granary was preached. Then followed the 1939–45 war, with a tremendous demand for all-out agricultural and industrial production Science and technology had made a marvellous record of increasing the efficiency of agricultural production between 1918 and 1939 with the result that we were able to export enormous quantities of food, feeds and many other agricultural products.

Once again, however, there are surpluses in some countries and acute shortages in others Are scientists to be blamed for the fluctuating demands and attitudes? They were not responsible for the events that caused the fluctuations and should not be criticized for having done what society demanded of them in times of crisis, especially when many scientists tried to help maintain perspective with respect to long term trends Are scientists to be blamed for the maldistribution of the means of subsistence and the barriers to exchange? Lack of a scientific attitude towards problems of human subsistence was to blame, not science and scientists

The development of atomic energy is another example Curiosity had prompted scientists to study atomic energy for some time before the 1939–45 war brought the demand for more effective weapons The greatest scientific and technological project in history was organized, the atomic bomb was developed, and now scientists are charged by many people with having shown civilization how to commit quick and effective suicide Scientists did not create the situation which led to the development of atomic energy for destructive purposes, and it is grossly unfair to charge them with responsibility for having met the demands of society to invent instruments of war to shorten the war

CIVILIZATION ON TRIAL

So we are again told that civilization is on trial and that science is largely to blame. There even are suggestions that there should be a moratorium on science until man is ready spiritually to utilize properly the facts and techniques of science.

Is civilization really on trial? Certainly it is! If civilization is measured by the degree of intellectual enlightenment and spiritual refinement attained by human beings, then civilization always has been on trial and always will be Civilization is not blueprinted and then projected into the future with automatic and guaranteed controls, its course depends upon human evolution as directed by human intellects and human emotions There is no statute of limitations on the trials of civilization There has been much progress, and sometimes there is retrogression, partly fancied and partly real, for, as H GREELLY said 'The illusion that times that were are better than those that are, has probably pervaded all ages' History is full of examples of nostalgia for the good old days, because time is likely to be so kind to the past as to create a desire to set back the hands of the clock and recapture lost values

Trials and temptations of civilization are inherent also in man's evolution As man progressed from a nomadic to an agricultural life, to industrialization and complex commercial relations, the complexity of his social and political relationships also increased and created new needs and new problems New inventions and new social organizations often require wider adjustments and readjustments, with a reorientation of attitudes The consequences of certain decisions often are inexorable Irreversible changes may occur, and society must bear the consequences of its decisions The realization of ambitions is often incompatible with the preservation of cherished values Peoples have adopted courses of action without reckoning their consequences, then have complained that civilization was deteriorating because they could not have what they had lost or thrown away Surely a scientific attitude can conduce to wisdom of choice and maintenance of perspective regarding trends

Not only is civilization always on trial, but the record is that many civilizations have failed, even the vaunted western civilization has several times been on the brink Was it the fault of science? Record shows that it was not. Was science, for example, responsible for the Dark Ages? Truth is that lack of science rather than too much science was largely responsible. The authoritarianism that suppressed individual thought and stifled intellectual progress was as unscientific as dangerous It could be dangerous even today

Should there be a moratorium on science, as is sometimes facetiously or seriously proposed? The dire consequences of the virtual blackout of science in the Middle Ages are known to every casual student of history We smile indulgently when we recall that learned professors in the best universities solemnly but harmlessly taught that the elephant had no joints in its legs, that the legs of a fox were shorter on one side than the other, that old eagles periodically visited the fountain of youth to become young again We are inclined to wonder at the wide acceptance of the doctrine that the function of a learned mind was not to find out whether certain doctrines were true but to adduce arguments to prove that they were true The blackout of science had many tragic consequences also The abasement of the body to purify the soul, the reliance on miracle and fetish healing, and the consequent lack of sanitation, led to some of the most terrible disease epidemics in the history of mankind Perhaps the most tragic of all is the fact that much of the misery and many of the fears resulted from retrogression—in surgery, in sanitation, in engineering, in a natural and rational attitude toward life and problems of living If time blunts the acuteness of our realization of the inhumanity resulting from this historic moratorium on science we need only study the distressing situations in many scientifically backward countries today Is the modern world entirely free from the blighting effects of authoritarianism and its tendency to suppress freedom of inquiry and expression?

THE NEED FOR MORE SCIENCE

What is needed is not a moratorium on science but even more science and technology, particularly is there need for man to try to become objective with respect to himself and the group of which he is a part We need to emancipate ourselves from our own stupidity and ineptitude with respect to ourselves in social affairs Even though the methods of social sciences may not be as precise as in some fields of natural science, is it too much to hope that man can learn to substitute facts and principles for unsupported assertions and easy generalizations ? Can man learn to demand truth instead of designing propaganda ? Can statesmanship be substituted for politics ? Can intelligence, honesty, fearlessness and fairness be substituted for 'the strategy of party and lust for the spoils of office' ? Perhaps it is hard to be really objective about ourselves and our group and to apply the facts and principles of the social sciences, because man runs head on into his own ignorance, his prejudices, his selfishness, his greed, his narrow nationalism, and certain cherished scruples The emancipation of man from his baser self obviously requires science , but not only science, it requires ethics also

Science can help in improving mankind, but it cannot do the whole job Scientists in general are motivated either by personal ambition, by curiosity, or by desire to render social service Even though motives are often mixed, most scientists do try to render social service and help alleviate distressing situations , but science must have help, because there are certain limitations to the scientific method Men think but they also feel, and their thoughts and feelings often become badly mixed Does clear thinking necessarily result in right action ? The question 'Can science alone adjust morality to its powers ?' needs an answer The statements of J FISKE that 'There has been more progress in intelligence than in kindness' and 'Half the cruelty in the world is the direct result of the stupid incapacity to put one's self in the other man's place' are all too true, even today Why are they true ?

Science can contribute as much to the refinement of the spirit as to the enlightenment of the mind For is it not irrational and completely unscientific to ignore the facts and situations that make people and peoples act as they do ? Would we always be so ready to condemn other people and peoples if we studied their problems with scientific objectivity and based our judgements on facts instead of prejudices ? If we used as rigorous criteria of truth in human affairs as every good scientist uses in his science, would we tolerate the ethics of the trickster and the demagogue in human relations ? If we always faced the truth, would we be as Pharisaical as we often are ? Does not rigid insistence on truth help to develop a sense of justice and conduce to ethical conduct ? Science helps to humanize but science needs help in the humanization process There can be no moratorium on science

A moratorium is needed, but it is a moratorium on the conflict between science and the humanities that is needed for science, religion, music, art, history, and literature have values in the degree to which they make men happier, wiser and better The value of each varies with individual men All are valuable in so far as they illuminate the intellect, refine the spirit and stimulate useful and ethical conduct To promote truth, wisdom and justice is not the prerogative of any one guild The factors and forces in the evolution of the human intellect and spirit are varied and complex , and it is unscientific and unethical to deny to each its fair share of credit for its contributions

It would be futile to try to apportion blame for the mutual intolerance between some scientists and some humanists Perhaps each group understands too little of the aims and attitudes of the other , perhaps the aims within both groups are sometimes too limited Certain it is that some scientists must concentrate on limited objectives if their investigations are to be fruitful Do not some humanists also dedicate themselves to a search for the truth in a small sector of their chosen fields ? Those who intensify their search often must sacrifice their desire for scholarship to the determination to solve problems or to discover the truth , and yet it is their researches that furnish the raw materials for the scholarship of others

Humanity needs both the sciences and the humanities , both are humanizing to the extent to which they humanize There is need for more understanding and tolerance between scientists and humanists , properly motivated all are humanists and their joint contributions can accelerate man's evolution towards intellectual enlightenment and spiritual refinement

E C STAKMAN

Gas Absorption

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GAS absorption is an important unit operation in chemical engineering, particularly in the heavy chemical industry In the purification of coal gas and synthetic gas as well as in the manufacture of hydrochloric acid, sulphuric acid, nitric acid, soda ash and bleaching lyes, to mention only the most striking examples, gas absorption is the essential feature of the process Since the 'twenties extensive research has been carried out with the result that the knowledge of this unit operation has increased considerably

In this article the problems and results in this field from the standpoint of the research worker will be considered

The essential element in gas absorption is the mass transfer between two fluid phases, if necessary combined with chemical reactions The latter are mainly restricted to the liquid phase although, for instance in the manufacture of nitric acid, the chemical reaction may also occur in the gas phase

It will be understood that in such a heterogeneous process as gas absorption a large contact area is a primary requisite for rapid transfer

There are three ways in which a large contact area can be established

1 the liquid is brought in contact with the gas in the form of thin films (film scrubbers)
2 the liquid is dispersed in the gas in the form of minute drops (spray scrubbers)
3 the gas is dispersed in the liquid in the form of small bubbles (bubble scrubbers)

All apparatus applied in gas absorption practice is based on one of these three principles or on a combination of them

Here serious problems are encountered which have only been partly solved The first things to discover when dealing with a process of mass transfer are the size of the contact area and the way in which this size depends on the various conditions of the experiment

The most complete answer to this question can be given for apparatus of type 1 The simplest representative of this type is the wetted wall column, the contact area of which may be determined with great accuracy For packed columns the question cannot be answered so easily, since it cannot be exactly ascertained which part of the packing will be wetted For the sake of simplicity the contact area may be considered to be equal to the total area of the packing material In apparatus in which gases or liquids are dispersed, types 2 and 3, determination of the contact area is almost impossible

Only in the last few years has insight been obtained[1,2] into the conduct of gas bubbles during their formation in and ascension through liquids, although much work is still to be done in this field

In the following sections of this paper we shall mainly restrict our attention to the proper mechanism of gas absorption , and shall deal in turn with purely physical absorption and absorption combined with simultaneous chemical reactions

PHYSICAL GAS ABSORPTION

The essential factor of physical gas absorption is that the molecules to be absorbed are transported from the gas phase to the gas/liquid interface , they are then dissolved in the liquid and subsequently transferred from the phase boundary into the liquid phase proper

This transportation of molecules is effected partly by convection and partly by diffusion In an entirely viscous fluid the transport perpendicular to the main direction of flow is exclusively effected by diffusion With turbulent flow on the other hand there exist velocity components perpendicular to the main direction of flow which have a very active effect on transport towards the phase boundary

Since the Reynolds number is a measure of the ratio between convective and diffusive transport it is clear that the rate of transport will generally be a function of the Reynolds number of the fluid A customary illustrative but very schematic picture of a fluid flowing along a boundary plane is as follows

Imagine the fluid to be divided into an entirely turbulent and completely homogenized main body separated from the phase boundary by a laminarly flowing boundary layer The diffusion through the laminar barrier will then be determinative for rate of transport towards the phase boundary , the Reynolds number is a measure of the thickness of this boundary layer and the higher this number the thinner the boundary layer

The picture given is undoubtedly too simple ; nevertheless it lends itself immediately to a quantitative treatment of mass transfer and leads to results by which the empirically observed phenomena are remarkably well interpreted.

In the boundary layer the conditions are those of a steady supply of the component A at a plane y_1 with steady removal at the same rate at a plane y_2. In addition to the component A there is present a second component Z which is neither supplied nor removed. Here Stefan's expression

$$N_A = \frac{D}{y_2 - y_1}(C_A + C_Z)\ln\frac{C_{Z_2}}{C_{Z_1}} \qquad (1)$$

is valid, where N_A is the number of mol transported per unit of area per second, D is the diffusivity, C_A and C_Z are the concentrations with respect to the components A and Z.

This may be written as follows

$$N_A = \frac{DC_{Z+A}}{y_2 - y_1}\frac{RT\ln(C_{Z_2}/C_{Z_1})}{RT} \quad \frac{DC_{Z+A}}{y_2 - y_1}\frac{\Delta\bar{G}_Z}{RT} \qquad (2)$$

where $\Delta\bar{G}_Z$ is the gradient of the molal free energy of component Z in the layer under consideration. From this it ultimately follows that an entropy difference acts as the driving force in the transport of molecules.

For small concentrations of A equation 1 may be replaced by

$$\begin{aligned} N_A &= \frac{D}{y_2 - y_1}\frac{C_Z + C_A}{C_{ZM}}(C_{A_1} - C_{A_2}) \\ &\triangleq \frac{D}{y_2 - y_1}(C_{A_1} - C_{A_2}) \qquad (3) \end{aligned}$$

where C_{ZM} is the logarithmic mean concentration of Z within the layer.

It is clear from the foregoing that mass transfer is governed by three factors:

a the so-called driving force $C_{A_1} - C_{A_2}$, *i.e.* the concentration gradient of component A in the layer considered

b the surface area

c the thickness of the stagnant layer $(x_2 - x_1)$

Applying this to transport in the boundary layer, effective thickness x, while considering a unit of area, we arrive at the following expression

$$N_A = \frac{D}{x}(C - C_i) = k\,(C - C_i) \qquad (4)$$

In equation 4 the suffix *i* refers to the phase boundary, C denotes the concentration in the main body of the fluid kg mol/cu m, C_i is the concentration at the gas/liquid interface, kg mol/cu m, k is the coefficient of mass transfer, given by

$$k = \frac{D}{x} = \frac{\text{diffusivity}}{\text{effective thickness of boundary layer}} \qquad (5)$$

It is customary to use the difference in partial pressure between the solute in the main gas stream and the solute at the liquid/gas interface $(p - p_i)$ as the driving force in the gas phase, the difference in concentration $(C_i - C)$ on the other hand being applied as such in the liquid phase.

From this it follows that for the mass transfer from the main body of the gas phase to the phase boundary the following expression will be valid

$$N_A = k_g\,(p - p_i) \qquad (6)$$

and for the mass transfer from the interface to the main body of the liquid phase

$$N_A = k_L\,(C_i - C) \qquad (7)$$

k_g and k_L respectively being the coefficients of material transfer in the boundary layers of gas and liquid expressed in kg mol/(sec) (sq m) (atm), kg mol/(sec) (sq m)(kg mol/cu m) respectively.

Since no material can accumulate at the phase boundary, for the situation considered is stationary, equations 6 and 7 will be identical.

Furthermore it is known that at the interface the distribution equilibrium between gas and liquid is established immeasurably rapidly, so that C_i and p_i will be interdependent because of the laws of phase equilibrium *e.g.* the law of Henry

$$C_i = Hp_i \qquad (8)$$

where H is Henry's constant.

From equations 6, 7 and 8 we can easily derive the following expression for the differential absorption rate

$$N_A = \frac{1}{(1/k_g) + (1/Hk_L)}\left(p - \frac{C}{H}\right) = K_g\,(p - p_L) \qquad (9)$$

where K_g is the absorption coefficient, which consequently is a function of the coefficients of mass transfer, $p_L\ (= C/H)$ is the equilibrium pressure of the dissolved component over the liquid.

In actual practice the integral rate of absorption N will be measured. By means of an exact integration equation 10 may be derived

$$N = K_g a\left(p - \frac{C}{H}\right)_M V = K_g a\,\Delta p_M\,V \qquad (10)$$

where V is the volume of the washer and a is the specific area of interphase contact, sq m/cu m of packed volume.

The suffix M denotes the logarithmic average of the driving force $[p - (C/H)]$ through the entire washer and is found by calculating the average of $[p - (C/H)]$ for the entrance and exit section of the washer.

In this connection it must also be stated that the efficiency η of absorption *i.e.* that fraction of the component to be absorbed which is effectively removed, depends on the absorption coefficient and the operating variables in the following manner[8]

$$\eta = \eta_{th}\frac{1-\exp\left[-\alpha(1-\beta)\right]}{1-\beta\exp\left[-\alpha(1-\beta)\right]} \qquad (11)$$

η, η_{th}, α and β are dimensionless numbers of the following quantities

$$\eta = \frac{p_0 - p_e}{p_0} \qquad \eta_{th} = \frac{p_0 - C_0/H}{p_0}$$

$$\alpha = \frac{K_G a V}{G} RT \qquad \beta = \frac{G}{HL}\,\frac{1}{RT} \qquad (12)$$

where G is the gas flow rate and L is the liquid flow rate, cu m/sec, η_{th} is the theoretical efficiency, p_0 the partial pressure in the entering gas and p_e the partial pressure in the exit gas (atm), C_0 the solution concentration in the entering liquid (kg mol/cu m), see *Figure 1*.

Equation 11 is plotted in *Figure 2*, by means of this graph the efficiency of the absorption for any working condition may be predicted, provided that K_G and a are known Hence it will be clear that the detection of the relationships between the absorption coefficient and the operating variables has been the object of a large number of investigations

Before going further into this matter, consider the relationship

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{Hk_L} \qquad (13)$$

From this it follows immediately that at high values of H, as with very soluble gases, it is possible that $Hk_L \gg k_G$, resulting in $K_G \simeq k_G$

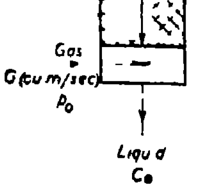

Figure 1 Schematic view of apparatus

In a similar case the rate of absorption is almost entirely determined by the mass transfer in the boundary layer of the gas phase Since the thickness of this layer depends upon the superficial linear gas velocity v (m/sec) the rate of absorption is considerably influenced by the gas velocity $k_G \propto v^{0.8}$

If on the other hand H is very small, as with slightly dissoluble gases, it is possible that $Hk_L \ll k_G$ or that $K_G \simeq Hk_L$ Now the rate of absorption is determined by the mass transfer through the liquid phase boundary layer and consequently depends on the superficial linear liquid velocity u $k_L \propto u^n$ This different behaviour of readily and slightly dissoluble gases makes it possible to determine k_G and k_L independently

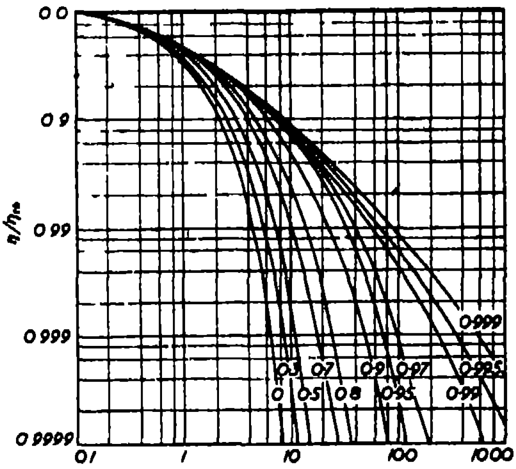

Figure 2 Absorption efficiency as a function of α and β The figures denote the value of β

For moderately dissoluble gases $1/K_G$ may be plotted against $(1/v)^{0.8}$, whence k_G may be derived from the slope of the curve obtained, k_L being derived from the intercept on the ordinate *Figure 3* shows a plot of $1/K_G a$ against $(1/v)^{0.8}$ for ammonia

The K_G value should be determined at a variable gas velocity but at a constant liquid velocity

It has already been remarked that the thickness of the boundary layer through which the diffusion takes place is determined by the degree of turbulence of the fluid, the Reynolds number R_e, which is a criterion for the ratio between the convective forces and the viscous forces in the fluid, being of great importance for this calculation

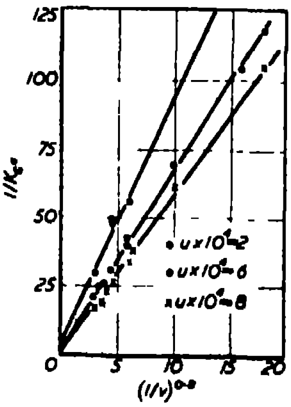

Figure 3 Results of Kowalke, Hougen and Watson with ammonia absorption

Furthermore it is understood that the mobility of the molecules to be absorbed with respect to the mean mobility of all molecules proves to be a factor of importance in this connection

A measure for the said ratio is provided by the Schmidt number

$$S_c = \frac{\nu}{D} = \frac{\mu}{\varrho D} \qquad (14)$$

where ν is the kinematic viscosity $= \mu/\varrho$, D being the diffusivity (sq m/sec), μ the viscosity (kg/m sec) and ϱ the density (kg/cu m)

Hence it is obvious that practically all empirically determined expressions denote a functional relationship between the coefficients of mass transfer and diffusivity, which at the same time contains the numbers of Reynolds and Schmidt and can usually be written

$$k \propto D\, R_e^{m}\, S_c^{n} \qquad (15)$$

Coefficients of mass transfer— Let us first consider the investigations dealing with the coefficients of mass transfer in the gas phase

The best known relationship in this field is the one proposed by E R GILLILAND and Γ K SHERWOOD[4] for the wetted wall column

$$\frac{k_G RTd}{D_G}\frac{p_{BM}}{P} = 0.024 \left(\frac{vd\varrho}{\mu}\right)_G^{0.83} \left(\frac{\mu}{\varrho D}\right)_G^{0.44} \qquad (16)$$

P being the total pressure, atm, d the internal diameter of the wetted wall column and p_{BM} the partial pressure of the carrier gas in atm

This relationship holds for a turbulent flow A recent investigation carried out by D W VAN KREVELEN and P J HOFTIJZER[5] deals with mass transfer in wetted wall columns in the field of laminar and pseudo-turbulent flows

A great number of measurements of the coefficients of mass transfer for turbulent flow along surfaces of different shapes was carried out by R W POWELL[6]

For packed columns no analogous relationship has been found so far giving a quantitative description of all variables concerned A non-dimensionless relationship which gives a reasonably satisfactory correlation of the experimental data is

$$k_G = 10\, \frac{D_G}{RT}\frac{P}{p_{BM}} \left(\frac{v\varrho}{a_p\mu}\right)_G^{0.8} \left(\frac{\mu}{\varrho D}\right)_G^{0.4} \qquad (17)$$

a_p being the area of packing material, sq m/cu m of packed volume

A number of investigators[7, 8] consider k_G also to be influenced by the liquid velocity According to D W VAN KREVELEN, P J HOFTIJZER and C J VAN HOOREN[8] the influence of the liquid velocity u (irrigation density) can however be explained from the fact that wetting will be insufficient for irrigation densities of 10^{-4} m/sec. This is clearly illustrated by *Figure 4* in which a number of experiments by O L KOWALKE, O A HOUGEN and K M WATSON[7] are represented It proves that the wetted fraction of the surface is given by the relationship

$$\frac{a}{a_p} = 1 - \exp\,(-\,\text{const}\ u) \qquad (18)$$

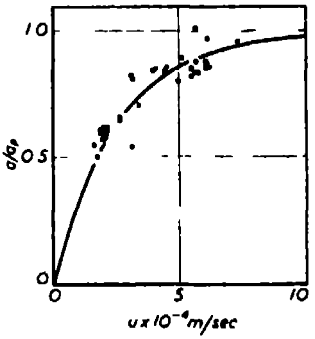

Figure 4 Fractional surface wetting as a function of superficial liquid velocity according to Kowalke, Hougen and Watson

Some measurements on the mass transfer in spray towers have been carried out by A W HIXSON and C E SCOTT[10] With respect to the values of $k_G a$ in bubble towers only few data are available[11, 12]

From the foregoing it may be concluded that k_G is only slightly dependent on the temperature For conditions of constant mass flow rate we find

$$k_G \propto \frac{D_G^{0.6}}{\mu_G^{0.4}\varrho_G^{0.4}}\frac{1}{T} \propto \frac{T^{0.9}}{T^{0.3}\,T^{-0.4}\,T} \propto T^{0} \qquad (19)$$

With respect to the coefficient of mass transfer in the liquid boundary layer our knowledge is even less complete than in the above Van Krevelen and Hoftijzer[5] have dealt with mass transfer in the liquid boundary layer, measured in a wetted wall column the relations given by them, however, are restricted to viscous *flow* T K SHERWOOD and F A L HOLLOWAY[13] carried out an interesting investigation on packed columns, the results of which may satisfactorily be represented (see *Figure 5*) by the expression

$$k_L = 6\;10^{8}\, D_L \left(\frac{u\varrho}{a_p\mu}\right)_L^{\frac{2}{3}} \left(\frac{\mu}{\varrho D}\right)_L^{\frac{1}{3}} \qquad (20)$$

As regards spray and bubble scrubbers only some relevant data are available[11, 12, 14]

From equation 20 it may be concluded that in turbulent films k_L will be very dependent on temperature, since

$$k_L \propto \frac{D^{0.67}}{\mu^{0.33}} \propto \frac{\left(\exp - \dfrac{E_{visc}}{RT}\right)^{0.67}}{\left(\exp \dfrac{E_{visc}}{RT}\right)^{0.33}} \propto \exp\left(-\frac{E_{visc}}{RT}\right) \qquad (21)$$

where E_{visc} is the activation energy of the molecular movement in the liquid according to EYRING ;

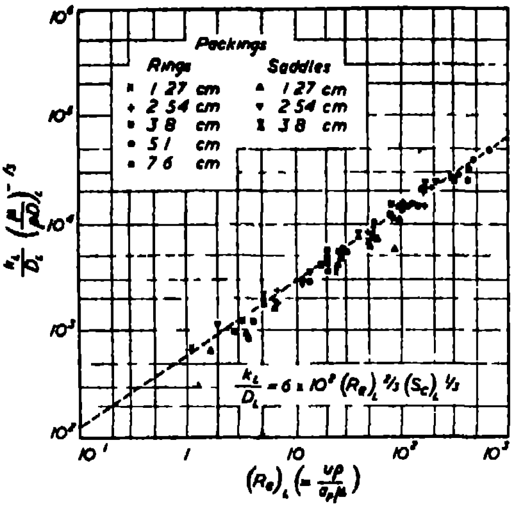

Figure 5 Experiments of Sherwood and Holloway

for water its value amounts to approximately 5,000 cal/mol

This strong dependency on temperature is in agreement with experiment[15]

CHEMICAL ABSORPTION

Now we shall proceed to a discussion of the problem of kinetics of a gas liquid reaction We shall only consider the relatively simple irreversible bimolecular reactions of the type

$$A + B \rightarrow R + S \qquad (22)$$

The reactions of practical importance generally occur in the boundary layer of the liquid Some of these reactions proceed so rapidly that they occur at the interface, with others the zone of reaction extends over a great part of the boundary layer

Consequently the situation is as follows a gaseous component A is carried to the interface by means of the normal convective and diffusive transport, where it dissolves and subsequently, during diffusion through the boundary layer, reacts with the second component B entering the boundary layer from the main body of the liquid phase, see *Figure 6*

The first investigator to deal with this problem was S HATTA[16], who in his mathematical treatment made use of considerable simplifications . he considered a reaction of the first order, consequently his solutions have no practical value

In recent articles by van Krevelen *et alii*[17, 18] the problem has been further worked out

The velocity at which the reaction now proceeds depends on three factors

1 the transport velocity of A in the boundary layer

2 the transport velocity of B in the boundary layer

3 the reaction velocity proper of A and B in the boundary layer

The complicated theoretical derivation[17, 18] of the final relationship for rate of absorption will not be discussed here the mathematical problem resolves itself into the solution of a differential equation of the second order

$$D_A \frac{\partial^2 A_c}{\partial x^2} = D_B \frac{\partial^2 B_c}{\partial x^2} = k\, A_c B_c \quad .. \ (23)$$

where A_c represents the solute concentration, expressed in kg mol/cu m, and B_c the concentration of B, kg mol/cu m

We shall give here a qualitative approximation of the results of the calculation As a measure for *1* the product $k_L A_i$ ($= M_1$, the characteristic rate of mass transfer of A) may be considered i e the optimal transport velocity of component A through the boundary layer, if diffusion is the only factor involved A_i is the solute concentration in the liquid at the gas/liquid interface, kg mol/cu m

In the same way the product $k_L B_L$ ($= M_2$ the characteristic rate of mass transfer of B) may be used as a measure for *2*, namely the optimal transport velocity of B through the boundary layer as a result of pure diffusion

Finally, the product $k\, A_i\, B_L\, x_L$ ($= Q$, the characteristic rate of the reaction) is a measure of *3* . it is the highest reaction velocity in the boundary layer which can be imagined B_L is the concentration of component B in the main body of the liquid, expressed in kg mol/cu m and x_L is the effective thickness of the liquid phase boundary layer

In the light of the foregoing it is obvious that according to theory the differential rate of absorption

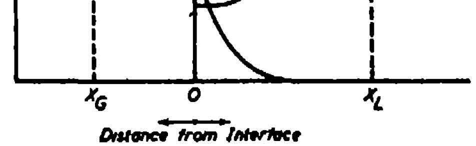

Figure 6 Concentration diagram for absorption with simultaneous (moderately rapid) chemical reaction f = film boundary, I = interface

per unit of interfacial area N_A is a function of M_1, M_2 and Q. In *Figure 7* this relationship is represented graphically; for this purpose M_1 has been selected as a standard rate so that N_A/M_1 has been plotted as a function of Q/M_1 for the various values of M_2/M_1.

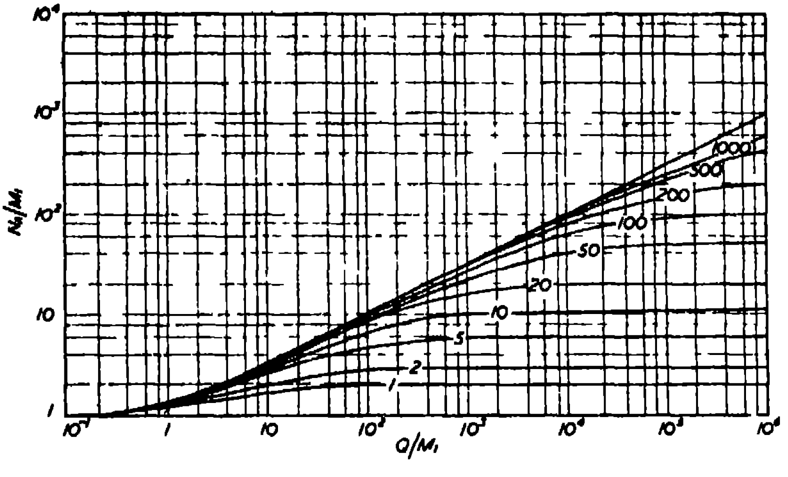

Figure 7 Graphical representation of chemical absorption Values of M_2/M_1 are given on curves

In a certain sense the ratio N_A/M_1 is the factor denoting how many times the gross rate of absorption is greater than the rate of physical absorption in other words it is the acceleration of the absorption as a result of the chemical reaction

From *Figure 7* a number of interesting conclusions may be drawn

As long as Q, or Q/M_1, is small, N_A/M_1 is approximately equal to 1, this means that the absorption proceeds practically at the same rate as diffusion of A through the boundary layer

When Q increases N_A increases also At a small value of k_2 (slow reaction) B_L being large (great excess of B), N_A may reach values located on the line

$$\frac{N_A}{M_1} = \left(\frac{Q}{M_1}\right)^{\frac{1}{2}} \text{ or } N_A = (QM_1)^{\frac{1}{2}} = (k_2 A_i^2 B_L D)^{\frac{1}{2}} \qquad (24)$$

in other words, the rate of absorption becomes proportional to the root of the concentration of B in the main body of the liquid, and is independent of the thickness of the boundary layer so that it will be independent of the liquid velocity k_2 is the reaction velocity constant.

If on the other hand k_2 is great (fast reaction) B_L being relatively small (insufficient excess of B) the rate of diffusion of B becomes determinative for the rate of absorption In *Figure 7* this is proved from the horizontal part of the curves. It will be seen that here $N_A = M_2$ Since M_2 depends on the thickness of the boundary layer, the rate of absorption is strongly influenced by the liquid velocity.

All the above is confirmed by experiment Examples of very fast reactions, in which $N_A = M_2 = k_L B_L$, are the neutralization reactions (absorption of hydrogen sulphide in alkaline liquids, absorption of ammonia in acid solutions), and the absorption of carbon monoxide in ammoniacal copper solutions. Characteristic examples of slow reactions, for which consequently equation 24 is valid, are the absorption of ethylene in sulphuric acid and of oxygen in ammoniacal copper solutions

An intermediate position is adopted by the moderately fast reactions the absorption of carbon dioxide in alkaline and ammoniacal liquids

In addition to the foregoing, for very fast reactions, the transport of component A through the boundary layer in the gas phase may play a part and may even become determinative A brief discussion of this phenomenon will consequently not be out of place

In *Figure 8* a and b, the concentration diagram has been plotted for a reaction which proceeds at an immeasurable rate When the excess of B is sufficiently great the case represented by *Figure 8a* arises. the reaction proceeds entirely at the phase boundary. However when an insufficient amount of B is available at the phase boundary, A can penetrate into the liquid and we have the situation represented by *Figure 8b* the (immeasurably narrow) reaction zone, running parallel to the phase boundary, is located within the boundary layer of the liquid

Mathematically this can be treated in a very simple manner For transport in the gas phase equation 25 is valid

$$N_A = k_G (p - p_i) \qquad (25)$$

For transport in the liquid phase it may be seen from *Figure 8b* that

$$N_A = \frac{D_A}{x_1} A_i = \frac{D_B}{x_2} B_L \qquad (26)$$

$$\text{where } x_1 + x_2 = x_L \qquad (27)$$

x_1, being the effective thickness of the liquid phase boundary layer from gas/liquid interface to reaction zone and x_2 the effective thickness of the liquid

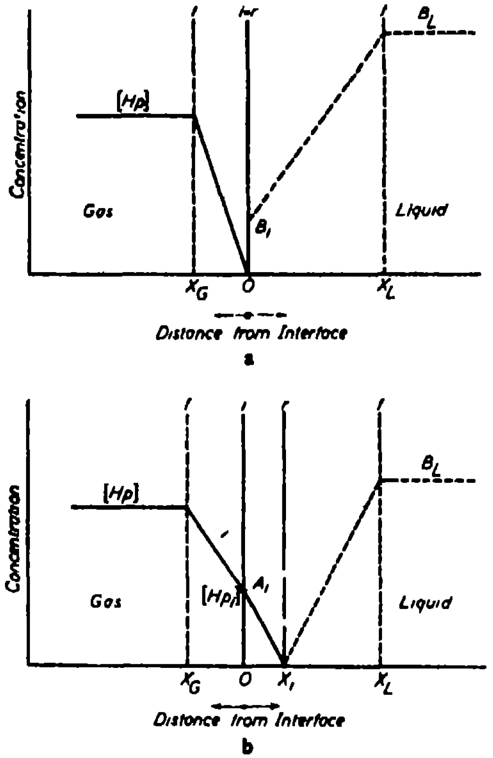

Figure 8 Concentration diagrams for absorption with simultaneous (very fast) chemical reaction a *excess of component B,* b *insufficient amount of B at phase boundary, f = film boundary, i = interface, r = reaction zone*

phase boundary layer from reaction zone to main body of liquid

When equations 25 and 26 are worked out for $D_A \simeq D_B \simeq D$ we find the following relationship for the differential rate of absorption

$$N_A = \frac{1}{(1/k_G) + (1/Hk_L)}\left(p + \frac{B_L}{H}\right) \qquad (28)$$

From the fact that $p_i \geqslant 0$ it naturally follows that

$$p \geqslant \frac{B_L k_L}{k_G} \qquad (29)$$

Here *Figure 8*b holds

If equation 29 is not satisfied we have

$$N_A = k_G p \qquad (30)$$

when *Figure 8*a holds

The important consequences of this reasoning will be evident as long as component *B* is present in great excess, the rate of absorption is determined by equation 30 and is only influenced by the gas velocity However as soon as equation 29 is satisfied the influence of the liquid velocity will increase, see equation 28 For gases which cannot easily be dissolved (small *H*-value) it may be that the influence of the gas velocity disappears altogether

It is even possible that in one and the same apparatus both relationships for the differential rate of absorption, equations 28 and 30, are observed, namely 30 in the upper section of the apparatus and 28 in the lower one The integral rate of absorption is then apparently governed by very complicated relationships, in fact, however, the problem is simple and may be reduced to equations 28 and 30

In a recent paper[19] all these examples of chemical reactions are described and compared with experimental data

CONCLUSIONS

From the survey on physical gas absorption it is obvious that our empirical knowledge is still far from complete on many points The wetted wall column has been the subject of most investigations As regards the packed column we have not yet succeeded in finding a satisfactory dimensionless relation for the coefficient of mass transfer as a function of the operating variables. Even less knowledge has become available about the relationships with spray and bubble washers

Furthermore an urgent need is felt for a more profound theoretical knowledge The problem of the nature of the influence of the Reynolds and Schmidt numbers as observed empirically has only partly been solved Furthermore we feel the lack of a satisfactory theoretical treatment of the degree of irrigation as a function of operating variables in the packed column, this may also be said about the mechanism of gas bubble and drop formation in bubble and spray washers

Generally speaking, the problem of the kinetics of chemical absorption has been solved in principle Here also however we are still faced with many difficulties *e g* in the fields of the reversible reactions and the more complicated reaction mechanism, for instance, simultaneous reactions in the gas and liquid phase.

In actual practice the research work of the last twenty five years has led to the important result that on the basis of present understanding a few measurements with a particular apparatus will usually be sufficient to make extrapolations for changed conditions with reasonable accuracy Also it is possible to calculate with satisfactory accuracy full scale columns, using measurements carried out in semi-technical apparatus.

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Gram Staining Reaction for Micro-organisms

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THROUGHOUT all branches of bacteriology and microbiology it is probable that no single staining reaction is so frequently used as the Gram reaction Discovered in 1883–84 by the Danish pathologist, H C J GRAM[1], the staining reaction was developed empirically for the differentiation of bacteria in infected tissues It would appear that in his original method Gram used aniline oil and gentianviolet to stain the nuclei of sections of nephritic kidney followed by Lugol's iodine to obtain a yellow staining of casts Dehydration with ethanol, however, completely decolorized the preparations Sections of pneumonic lung, treated in the same way, showed micrococci which retained the blue stain Micro-organisms which similarly remained stained after extraction with ethanol were observed also in cases of tuberculosis, anthrax, pyaemia and erysipelas Gram further records that the presence of micro-organisms, such as the typhoid bacilli, which were decolorized with ethanol, could be demonstrated by the use of a counterstain of contrasting colour, such as bismarck brown

With application of the technique to general bacteriology, organisms of the first group came to be known as 'Gram positives', those of the second as 'Gram negatives', whereas organisms particularly susceptible to small variations in the staining technique, and thus with intermediate staining properties, were called 'Gram variables'.

It is now realized that the reaction of bacteria to the Gram staining technique is correlated with so many biological differences that the division into Gram positive and Gram negative species must necessarily correspond to some fundamental differences in the structure, chemical nature and physical behaviour of the individual cells

In principle the Gram technique in its present form consists essentially in staining fixed smears with an aqueous solution of a dye of the *para*rosaniline series and mordanting with aqueous iodine Subsequent washing of the preparation with ethanol or acetone removes the dye from the Gram negative organisms, whereas the Gram positive retain the stain. Differentiation is rendered more obvious by counterstaining with an acid fuchsin dye of contrasting colour It is apparent that such a sequence of staining reactions demands a standard technique Several modifications of the method are available which may not give strictly comparable results For the Gram reaction to have its full significance it would appear that such factors as the type of fixation, the duration of staining, the nature of the mordant, the nature of the decolorizing agent and the time in which it is in contact with the cells should be standardized Furthermore, retention of the Gram positive stain is not a constant property of a given cell but, within limits, varies with such factors as the age of the culture and the nature of the culture medium.

The ability to retain the Gram positive stain appears to be a specific property of bacteria and yeasts only. Modifications of the method have been used for staining chromosomes[2, 3] but, in general, cells of animal or vegetable origin do not retain the stain

MECHANISM OF THE GRAM REACTION

As the various theories which have been proposed to explain the mechanism of the Gram reaction have been reviewed in considerable detail both by R J DUBOS[4] and more recently by M WELSCH[5], it is proposed in this review to give consideration only to studies which have contributed materially to an understanding of the fundamental differences, both in structure and function, which exist between the Gram positives and the Gram negatives

In stained smears of Gram positive organisms individual cells may be observed which appear Gram negative, and the incidence of these Gram negative forms increases with the age of the culture E DEUSSEN[6] observed that this transformation from Gram positive to Gram negative could be effected by acids and alkalis, and by autolysis Yeast cells became almost completely Gram negative when extracted with 2-4 per cent sodium hydroxide, and subsequently became considerably shrunken when washed several times with water[7] Deussen also recorded that salts of nucleic acid diffused through the cytoplasmic membrane of these distorted cells so that their original Gram positive state was partially restored

It was observed by J D CHURCHMAN[8] that suspensions of *Bacillus anthracis* became Gram negative when brought into contact with small amounts of gentianviolet or acriflavine These Gram negative forms appeared thinner than the original Gram positive cells and the cell-free filtrates from such preparations were assumed to contain proteins since they gave a positive reaction with ninhydrin On the basis of these observations Churchman postulated the existence of a Gram positive cortex and a Gram negative medulla

Similarly N GUTSTEIN[9], by the application of a series of staining and mordanting techniques, reached the conclusion that the ectoplasm of the Gram positive cell was composed of a basic substance in combination with an acid lipid, and that this complex was responsible for the retention of the Gram stain.

The concept that Gram positive micro-organisms contained a complex structure at or near the cell surface which was responsible for the retention of the positive stain, was considerably strengthened by R. J DUBOS'[10] work on pneumococcal autolysis, to be discussed in more detail later. In these studies the observation was made that before cellular disintegration occurred, the autolysing pneumococci first became Gram negative. An analysis of the material liberated into solution when a suspension of Rough pneumococci type *II* was allowed to autolyse at 37°C and at *p*H 7 until Gram negative, revealed the presence of a ribonucleoprotein and ribonucleic acid[11, *cf* 9] It was also found that by a similar process of controlled autolysis it was possible to release from staphylococci a substance which gave the reactions of ribonucleic acid

The full significance of these observations was realized when it was shown by H. HENRY and M. STACEY[12] that suitable Gram positive bacteria and yeasts could be 'stripped' of an essential component of their Gram positive material by extraction with 2 per cent sodium cholate at 60°C and thereby rendered Gram negative A fraction from the extract, which itself stained Gram negative, could be 'replated' on to the Gram negative cytoskeletons under reducing conditions, to restore the Gram positive staining characteristics Analysis of this fraction showed that it consisted essentially of magnesium ribonucleate, together with carbohydrate and traces of protein With exposure to air the cytoskeletons became irreversibly oxidized and, at the same time, lost their ability to recombine with magnesium ribonucleate Less complete recoupling occurred when magnesium ribonucleate was replaced by the sodium salt, and replating could never be achieved with salts of deoxyribonucleic acid, or with nucleosides or nucleotides

In these studies, which have mostly been confirmed by J. W BARTHOLOMEW and W W UMBREIT[13], the important observation was made that the reduced cytoskeletons of one extracted Gram positive organism could be recombined equally well with magnesium ribonucleate from the extract of the same or other Gram positive cells The fact that the nucleic acids are interchangeable suggests not only that the various bacterial ribonucleic acids show little, if any, structural differences, but also that there is a similarity in the chemical structure of that part of the cytoskeletons with which combination occurs Presumably, this receptive structure is destroyed or altered in some way when Gram positive cells are rendered Gram negative by enzymic methods, since the cytoskeletons obtained under these conditions fail to recombine with magnesium ribonucleate.

NATURE OF THE GRAM COMPLEX

From the observations described above, it was concluded that the Gram positive organisms differ from the Gram negatives in having, as part of their surface structure, the magnesium salt of ribonucleic acid[12]. It was further suggested that the Gram positive material in micro-organisms was a high molecular complex formed by the combination of a reduced basic protein in the cell cytoskeleton with the magnesium ribonucleate This latter complex was later isolated as a nucleoprotein containing magnesium and –SH groups from a number of Gram positive organisms by a procedure which involved a relatively short autolysis and, in its native form, was found to stain intensely Gram positive[14] Dissociation of the nucleoprotein gave ribonucleic acid together with some deoxyribonucleic acid, and a basic protein which contained arginine and –S–S– linkages Neither the nucleic acid nor the protein alone could be stained by Gram's method, but on re-forming the complex at *p*H 5 in the presence of magnesium ions and formaldehyde it again stained Gram positive

In these experiments it was found that in a series of Gram positive and Gram negative organisms the ratio of deoxyribonucleic acid to ribonucleic acid was considerably higher in the Gram negatives than in the Gram positives The same conclusion is also reached from a study of the results of A BOIVIN, R VENDRELY and R TULASNE[15]

Although the nucleic acid of the Gram complex was, in general, dissociated from its combination with other cellular constituents by the highly surface active sodium cholate, the essential component of the Gram complex of *B subtilis* was isolated, under these conditions, as a white, fibrous, protein-free solid, which contained both ribo- and deoxyribonucleic acids apparently in combination with polysaccharide[13]

Further evidence suggesting that the nucleic acid of the Gram complex is associated with polysaccharide was provided by a study of the action of lysozyme on heat-killed Gram positive organisms Lysozyme, the enzyme in egg-white which lyses living suspensions of certain saprophytic micro-organisms, particularly *Micrococcus lysodeikticus*, owes its action to the ability to hydrolyse certain polysaccharide components of the cells[16, 17] The lysis of susceptible Gram positive bacteria by lysozyme is preceded by a change in the staining reaction from Gram positive to Gram negative[18] Although killed Gram positive cells are more resistant to the action of lysozyme than are living cells, it has been shown that killed cells become Gram negative when incubated with lysozyme[19] It was observed that during this change from Gram positive to Gram negative, certain linkages in polysaccharide material located at the cell surface were hydrolysed, and undegraded ribonucleic acid was liberated from the cells Recent work by H. J WELSHIMER and C F ROBINOW[20] with *B megatherium* suggests however, that marked changes in permeability occur as a result of the action of lysozyme on carbohydrate components of the cell wall, and the observed change in the Gram staining reaction is due to the loss of ribonucleic acid from the cells by a process of diffusion

Although Gram negative bacteria contain relatively large amounts of ribonucleic acid[18] which is responsible for the basophilic properties of the cytoplasm[21], apparently they do not contain the surface 'ribonucleoprotein' constituent which characterizes the Gram positive organisms Indeed, Gram negative bacilli and cocci liberate a molecular complex consisting of phospholipid, protein and polysaccharide when extracted with a wide variety of reagents, and immunochemical analysis suggests that this complex is located at the cell surface[22] Thus it appears that Gram negative bacteria, although differing in immunological specificity, are characterized by a common organization of surface constituents

AUTOLYSIS OF GRAM POSITIVE BACTERIA

A step towards elucidation of the structure of Gram positive organisms has been made recently by a study of the enzyme systems involved in the autolytic disintegration of the cells[23] Earlier studies of bacterial autolysis were confined mainly to the pneumococcus, and revealed that the lysis of the cells was accompanied by proteolysis, resulting in an increase in both amino- and non-coagulable nitrogen, and by lipolysis liberating ether soluble fatty acids[24] Cell-free autolysates, containing the enzymes of the autolytic system, acted upon heat killed pneumococci to give results comparable with those from spontaneous autolysis and also brought about the partial lysis of suspensions of heat killed *Streptococcus viridans*[25] Further observations[10] revealed the significant fact that before lysis of the pneumococci occurred the cells first became Gram negative, and this change in the staining reaction was not necessarily associated with complete lysis of the cells It was possible, moreover, to effect this change in the Gram staining reaction of heat killed Gram positive pneumococci by the action of pancreatic ribonuclease[26] and a ribonuclease-like enzyme isolated from rabbit leucocytes[27] These enzymes, which have the common property of specifically hydrolysing ribonucleic acid, have been shown to render Gram negative a wide range of heat killed Gram positive micro-organisms[28].

Extension of the investigations of bacterial autolysis to other Gram positive organisms has shown, in agreement with Dubos[10], that it is possible to divide the autolytic disintegration of the cells into two separate and distinct stages, namely the change from Gram positive to Gram negative, and the subsequent lysis of the Gram negative cell bodies[23] The fact that the second stage of autolysis was inhibited by reducing agents made possible the isolation of the enzyme systems of the two stages The non-specific enzyme system responsible for the lysis of the Gram negative cell bodies was composed of a proteinase and a peptidase, and its action resulted in the complete disintegration of cellular structure, with little contribution to an understanding of cellular architecture This proteolytic system had no action on heat killed Gram positive cells and did not play any part in autolysis until the cells had become Gram negative

Detailed studies of the properties of the initial stage enzymes from both *Clostridium welchii* and *Staphylococcus aureus* revealed that the two were closely similar Although differing in several respects from the ribonuclease of animal tissues, they had in common the property of hydrolysing free ribonucleic acid, but not deoxyribonucleic acid These enzymes were species specific, and to some extent strain specific, in their action on heat killed Gram positive cells Since the ribonucleic acids of the Gram complex of various bacterial species do not show any fundamental structural differences[12], the specificity of these enzymes is apparently determined by some other component of the Gram complex, possibly the specific polysaccharide

LOCATION OF THE GRAM COMPLEX

The problem whether the Gram nucleoprotein is located at the surface or is contained within the cytoplasm of the Gram positive cell is of considerable interest In this connection the relative ease with which ribonucleic acid may be removed from suitable Gram positive cells with sodium cholate, together with the fact that the resulting Gram negative cytoskeletons, after reduction, accept magnesium ribonucleate to become Gram positive again within a few minutes, suggests that the nucleic acid is located at or near the cell surface

The work of J W BARTHOLOMEW[18] in which it was claimed that *Neisseria catarrhalis* became Gram positive within fifteen minutes when treated with magnesium ribonucleate in the presence of formaldehyde also suggests that the Gram positive material is located at the cell surface, since it is unlikely that, under these conditions, the nucleic acid molecule is able to penetrate into the cell These results, which require the existence [illegible] cell surface of a protein of particular structure which is capable of combining with nucleic acid to form a Gram positive complex, cannot, however, be accepted, since attempts to repeat the work have proved unsuccessful Furthermore, suspensions of both *N catarrhalis* and *N gonorrhoeae*, previously extracted with 2 per cent sodium cholate at 60°C, failed to combine with magnesium ribonucleate[19]

The action of enzymes reveals that considerable differences exist between the structures of Gram positive and Gram negative cells In general, killed Gram positive organisms are resistant to proteolytic enzymes, such as trypsin, provided these are free from ribonuclease activity[20], cf [19] Killed Gram negative organisms, on the other hand, are readily lysed by trypsin, as are also the Gram negative cell bodies which result from the action of ribonuclease on killed Gram positive organisms From this information it appears that in *killed* Gram positive cells the ribonucleic acid of the Gram complex is located at the cell surface Evidence which suggests that the nucleic acid is similarly located in living Gram positive cells follows from the fact that the change from Gram positive to Gram negative which occurs with the liberation of ribonucleic acid[19] when killed Gram positive cells are incubated with lysozyme also occurs as the initial stage of the lysis of living organisms by lysozyme[10] In the highly susceptible *Micrococcus lysodeikticus* it has been claimed[21] that the lysozyme substrate is apparently one of the antigenic components of the organism and presumably forms part of the cell surface

The application of immunological methods would, theoretically, enable the location of the Gram complex to be determined, since the intact bacterial cell reacts most readily, if not solely, with antibodies which are directed against those of its constituents exposed at or near the cell surface[22] Unfortunately, in contrast to Gram negative organisms, little is known of the nature of the complete surface antigens of Gram positive bacteria, and there appears to be no record of the isolation from the latter of a complete antigen whose serological specificity is due to a polysaccharide component[23] However, in view of the more recent information concerning the structure of the Gram complex, it is possible to interpret in more detail the results of the immunological analysis of the structure of pneumococcus[24]

Virulent pneumococci may be immunologically differentiated into a number of serological types which differ only in the chemical composition of the capsular polysaccharide Enzymes have been obtained from saprophytic soil micro-organisms which hydrolyse specifically the capsular polysaccharides of the pneumococci without affecting either the viability of the organisms, their Gram staining properties, or their capacity to reproduce, under favourable circumstances, the type specific capsular material[25] The fact that the enzymes are active against living pneumococci shows that the capsular material is not an essential structure of the living cell Simultaneously with the loss of the capsular material, which occurs when living virulent pneumococci are treated with the specific polysaccharidases, the organisms largely lose their ability to agglutinate in specific antiserum[25] Although these polysaccharides determine the immunological specificity of the pneumococci, they are not themselves antigenic This fact suggests that in the living cell the polysaccharides are linked with other constituents to form the complete antigen

When the ribonucleic acid component of the Gram complex of pneumococci is hydrolysed either by ribonuclease or by the ' ribonuclease ' of the pneumococcus autolytic system, the cells become Gram negative and somewhat smaller in size In each instance the change in the staining reaction, although not affecting the morphology of the cells, results in a loss of type specific antigenicity Under these conditions the type specific capsular polysaccharide is liberated from the pneumococci in an undegraded form because it is precipitable by specific antiserum[15] It follows, therefore, that the loss of antigenicity is due to the destruction of a second component of the capsular antigen Since the loss of antigenicity occurs as a result of the specific action of ribonuclease on the ribonucleic acid of the Gram complex of pneumococci, it is possible that the capsular polysaccharide is in some way, linked to this complex This theory is supported by the observations that the specific polysaccharides obtained by complete autolysis of types *II* and *V* pneumococci contained as much as 5 per cent of a ribonucleic acid constituent in firm combination[16] Virulent pneumococci are differentiated from the avirulent variants only by the presence of the polysaccharide capsule surrounding the cells From this evidence it therefore appears that the Gram complex (of *Pneumococcus*) is located at the cell surface

From the foregoing discussion it appears essential at this point to give some consideration to the structure of the bacterial cell and, in particular, to the location of the surface constituents The living cell consists of a mass of cytoplasm which constitutes the main bulk of the cell and which contains the nuclear elements which take part in cell division Surrounding the cytoplasm is the cytoplasmic membrane and outside this is the cell wall on which such a structure as the capsule may be built[18] Normally, the cytoplasmic membrane, which is assumed to determine the properties of semi-permeability of the cell, is in close contact with the cell wall and cannot be differentiated from it The membrane may, however, be demonstrated by plasmolysis When bacteria are suspended in solutions of osmotic pressure higher than that of the cytoplasm, the latter shrinks and the cytoplasmic membrane is drawn away from the rigid cell wall In the writer's opinion, the very rigidity of the cell wall under the many diverse conditions which deform the cytoplasm suggests that it may be regarded as a porous structural framework which is more or less responsible for the maintenance of cell form The equilibrium between the internal and external environments of the bacterial cell is mainly determined by the semi-permeability of the cytoplasmic membrane and, in this sense, the cytoplasmic membrane constitutes a boundary between the internal and external structures of the cell

On this reasoning, it may well be that the Gram complex of the cell surface is either distributed throughout the interstices of the cell wall, or is located between the cell wall and the cytoplasmic membrane It does not appear to form part of the structure of the cell wall insofar as the latter can be demonstrated equally well in the cytoskeletons of cells rendered Gram negative with sodium cholate as in the intact Gram positive organism[9] Support for the second of the above hypotheses is provided by the following evidence Normal cells of *Saccharomyces cerevisiae*, when photographed in ultraviolet light, are found to contain some substance which adsorbs ultraviolet light of 2,650Å and which is associated with the outer surface of the cytoplasmic membrane The ultraviolet adsorption of this substance, together with the fact that it is removed when the yeast cells are rendered Gram negative by extraction with sodium cholate[12], suggests that it is the nucleic acid of the Gram complex

Furthermore it was claimed by B DELAPORTE[17] that ribonucleic acid was removed from yeast by merely washing the cells with water or dilute sodium bicarbonate It was further claimed that these cells from which most of the ribonucleic acid had been removed by the mild extraction procedures were capable of growth when placed in a suitable medium This evidence would apparently establish the existence of ribonucleic acid outside the cytoplasmic membrane, since the passage of the complex nucleic acid molecule through the cytoplasmic membrane of the living cell cannot be envisaged It seems desirable that this work, in view of its significance, should be repeated and extended to include the determination of total and viable counts since it appears more than likely that the ribonucleic acid isolated under these conditions was derived from dead cells in which partial autolysis had already taken place

From the information at present available, and without further contrary evidence, it seems feasible to assume that the Gram complex is located at the surface of the Gram positive cell Thus, it may well be that Gram positive, as well as Gram negative, organisms possess a common organization of their surface constituents The consequent differences in nature and composition which exist between the surfaces of Gram positive and Gram negative organisms result in the two groups exhibiting widely different physical as well as biological properties Of interest in this connection is the fact that the so-called ' isoelectric ' points of Gram positives occur around pH 2·0 and those of the Gram negatives around pH 5·0, whereas the 'isoelectric' points of the Gram variables fall between these values[38, 39]

MAGNESIUM REQUIREMENTS OF GRAM POSITIVE AND GRAM NEGATIVE ORGANISMS

Knowledge of the nature of the Gram complex has already led to results of some interest, particularly with regard to the magnesium requirements of Gram positive and Gram negative organisms Magnesium has recently been shown to be essential for the normal cell division of 'rod-shaped' eubacteria in complex media[40, 41] and under conditions of magnesium deficiency or excess these organisms were found to grow in the form of long filaments This inhibitory effect of higher magnesium concentrations on cell division is in accordance with the fact that enzymes which are activated by metallic ions in low concentrations are also inhibited by the same ions at higher concentrations[42] The magnesium requirements of the Gram positive organisms were found to be significantly greater than the requirements of the Gram negative organisms and this difference was attributed to the fact that the former incorporated magnesium into the structure of the Gram complex In support of this theory, the magnesium of Gram negative organisms and the Gram negative forms of Gram positives was entirely in the ionic form, whereas part of the magnesium of Gram positive cells was 'bound' by the Gram complex

Quantitative experiments in simple synthetic media composed of inorganic salts, a suitable nitrogen source and glucose or glycerol revealed that all of a series of eubacteria were incapable of growth in the complete absence of magnesium[43] It was also shown that the concentration of magnesium optimal for maximum growth varied according to the Gram reaction of the eubacteria, the magnesium requirements of the Gram positive organisms being some ten times greater than the requirements of the Gram negative species In contrast to the observations made in complex media, normal cell division occurred in cultures of the eubacteria in simple synthetic media containing sub-optimal amounts of magnesium To explain these differences the suggestion was made that in the development of a normal bacterial population, magnesium is essential both for the synthesis of essential metabolites intermediate in composition between the foodstuff provided and the bacterial protoplasm, and for cell division In a complex medium containing proteins, polypeptides and essential growth factors it is conceivable that some or all of these essential metabolites are normally present in the medium Under these conditions, therefore, a deficiency of magnesium would predominantly affect the process of cell division On the other hand, in a simple synthetic medium, magnesium is essential both for growth (in the sense of synthesis of cell substances) and cell division Under normal conditions of growth, synthesis must precede cell division and, presumably, requires the higher magnesium concentration That is at concentrations of magnesium below the growth optimum, normal cell division occurs throughout the restricted population that the medium is able to maintain Support for this hypothesis is forthcoming from the fact that in synthetic media containing a wide range of amino acids and growth factors, the growth of eubacteria is less dependent upon the magnesium concentration than is the process of cell division, and in such media containing small amounts of magnesium, filamentous forms of the 'rod-shaped' organisms are observed[44] The effect of the magnesium ion in the processes of cell division and synthesis appears reasonably specific, insofar as magnesium can be only partially replaced by manganese and other metallic ions of similar ionic radius[44]

NITROGEN METABOLISM OF GRAM POSITIVE AND GRAM NEGATIVE ORGANISMS

A further important difference between Gram positive and Gram negative bacterial species is revealed from a study of their nitrogen metabolism It has been pointed out by E F GALE[45] that among the Eubacteriales the organisms which can utilize ammonia as sole source of nitrogen are generally speaking Gram negative, whereas many Gram positive species require a wide variety of amino acids for optimal growth It has been shown[46] that certain Gram positive bacteria assimilate and accumulate certain amino acids in the free state within their internal environment Some amino acids, particularly lysine, pass into the cell by diffusion whereas others, notably glutamic acid, can only enter the cell as a result of an active process

The capacity to effect the concentration of free amino acids within the internal environment of the cell is confined to the Gram positive species[47] and free amino acids cannot be detected within the cells of Gram negative bacteria under any conditions tested There is little doubt that Gram negative cells can assimilate amino acids, but they cannot affect the internal concentration[48] It has been suggested that this property of Gram positive bacteria of assimilating free amino acids represents the first step in protein synthesis by these organisms, the concentration of the free amino acid within the internal environment compensating for the lack of synthetic ability towards such substances[48]

ACTION OF ANTIBACTERIAL AGENTS

Finally, mention must be made of the differential susceptibility of Gram positive and Gram negative species to different antibacterial agents Basic dyes and anionic detergents as well as penicillin and gramicidin are, as a rule, much more active against Gram positive than against Gram negative species On the other hand tellurites, azides and dichromates appear selective for many Gram negative organisms[49, 52] Undoubtedly, these differences are due in some cases to variations in the properties of surface constituents and in others to differences in the metabolism of the Gram positive and Gram negative organisms Thus, it has been demonstrated with living and dead yeast cells that acridines form adsorption complexes with nucleoproteins and in this way exert their antibacterial action by displacing catalytically active ions[53] The presence of the nucleoprotein at the cell surface, together with the greater magnesium requirements of the Gram positive organisms, points to the understanding of the greater susceptibility of the Gram positive organisms to these agents Of significance in this respect is the observation that the antibacterial effects of diamidines are inhibited by nucleic acids[54] Furthermore, the growth inhibitory effects of atabrine, 2-chloro-7-methoxy-5-(1-methyl-4-diethylamino-butyl)-amino-acridine, has also been shown to be inhibited by both calcium and magnesium[55]

The selective action of anionic detergents and the greater activity of cationic detergents against Gram positive organisms[56] may, in part, be due to the ability of these surface active agents to dissociate the Gram complex and, in part, to the protective action of the phospholipid component of the surface structure of Gram negative organisms[57, 58]

Penicillin has been found to block the assimilation of glutamic acid by Gram positive bacteria[59] and possibly also to interfere with the synthesis of the Gram complex[46], in addition, triphenyl methane dyes penetrate the cell and inhibit the internal metabolism of glutamic acid[48], and sulphathiazole interferes in some way with protein synthesis[60] It has been suggested that the greater sensitivity of the Gram positive organisms to these antibacterial agents is explained by the greater dependence of Gram positives on the ability to assimilate and concentrate free amino acids as opposed to the capacity of Gram negatives to synthesize these substances as and when required[45]

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Reaction between Nitrous Acid and Amines

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THE history of this subject commenced when in 1848 R PIRIA found that he could produce malic acid, a nitrogen-free compound, by the action of nitrous acid on asparagin[1], and shortly afterwards A STRECKER described a similar treatment of glycine[2] The reaction soon became generally recognized for the removal of amino groups

Further study revealed complications The net result of the treatment of a primary amine with nitrous acid is not, as a rule, the quantitative formation of the corresponding alcohol and nitrogen, several other products are formed In 1872, E LINNEMANN observed that the interaction of silver nitrite and *n*-propylammonium chloride gave *iso*propyl alcohol and nitrosodipropylamine in addition to *n*-propyl alcohol, but that the combined yield of these three products did not account for the whole of the propylamine[3] Soon afterwards V MEYER and F FORSTER verified Linnemann's observation and also identified propylene as a constituent of the gas evolved during the reaction[4] Similar results have since been obtained with *n*-butylamine and several other primary aliphatic amines[5, 6] These observations and the further one by O WALLACH that ring expansion can occur when alicyclic amines are treated with nitrous acid[7] reveal that there are complexities in the reaction which were not suspected by the earlier workers and which still lack a completely adequate explanation

The discovery of the diazo compounds by P GRIESS[8] was a direct outcome of Piria's earlier work Because the diazo compounds so soon found industrial application, the nitrous acid/amine group of reactions attracted considerable interest Nevertheless, surprisingly little fundamental work has been done on them

In a general examination of the problem of these reactions, a number of questions arise The secondary amines, both aliphatic and aromatic, also react with nitrous acid, giving nitrosamines It has to be decided whether the reaction here is fundamentally the same as, or different from, that of the primary amines Again, the nitrosation products of α-aminoketones and α-aminocarboxylic esters, which contain two adjacent nitrogen atoms, are neither nitrosamines nor diazo compounds of the aromatic type Their position in the general scheme must be considered Further, the many secondary reactions entered into by the primary products are a complicating factor in any investigation of the initial nitrous acid/amine reaction

PROPERTIES AND STRUCTURE OF NITROUS ACID

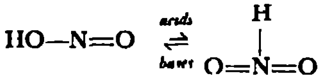
The dissociation constant[9] of nitrous acid is 0·00046 at 12·5°C It can therefore be regarded as a weak acid Its most notable property is its instability In aqueous solutions[10] of greater concentration than 0·2 N it decomposes rapidly and spontaneously at 25°C The decomposition in the absence of air is represented by

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

In air secondary changes also take place

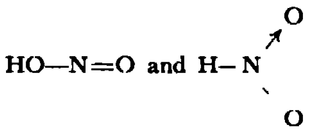
Quantitative studies in which nitrous acid is used as a reagent must be carried out under very carefully controlled conditions to minimize the complications arising from its decomposition

The actual molecular structure of the acid has been a matter for conjecture. It certainly ionizes to H^+ and NO_2^-, but some of its reactions are more readily interpreted as those of an undissociated molecule HO—N=O or even of a molecule tending to dissociate as a base into NO^+ and OH^-. For example, the ready esterification of nitrous acid by alcohols has been attributed to a reaction between the alcohol acting as an acid and the nitrous acid as a base[11]. H. KRALL suggested that the scheme

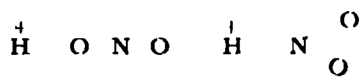


$$\mathrm{HO{-}N{=}O} \underset{bases}{\overset{acids}{\rightleftharpoons}} \mathrm{O{=}\overset{\displaystyle H \atop |}{N}{=}O}$$

explained many otherwise obscure observations[12]. This explanation recalls one of the older problems of structural organic chemistry, namely, the simultaneous formation of nitroparaffins and nitrous esters when the alkyl halides are brought into reaction with metal nitrites. This might be explained by the existence of two isomeric structures for nitrous acid, both giving rise to salts



However, on dissociation to give hydrogen ions, both these structures would give complementary anions of identical electronic structure



$$\overset{+}{\mathrm{H}}\quad \mathrm{O\ N\ O}\qquad \overset{+}{\mathrm{H}}\quad \mathrm{N}{\mathrm{O} \atop \mathrm{O}}$$

Therefore, in any reaction in which nitrous acid or the metal nitrites may take part in the form of their ions, the result would be the same whatever the structure of undissociated substance.

THE AMINES

In considering any reaction in which primary or secondary amines are involved, two factors must be considered

1 the salt-forming power of the amines

2 the reactivities of the hydrogens in the free amino group.

The measure of *1* is given by the electrolytic dissociation constants which have been determined for a large range of amines. A precise measure of *2* is more difficult to reach. There have been quantitative studies of the reactivity of various amines with selected reagents under standardized conditions, for example, benzoylation[13], or reaction with allyl bromide[14], but with the data available a comprehensive and precise assessment of this factor for a wide range of amines is not possible.

It is, of course, conceivable that the two factors would act together and that their magnitude would be affected in the same way by the structure of the rest of the molecule. Unfortunately, available evidence shows that such a simplification is inadmissible. Arguments on the relative influence of the two factors in any selected reaction are therefore restricted to a qualitative basis. Nevertheless, it is possible to arrive at some useful conclusions, as will be seen later, for the reaction of amines with nitrous acid.

AMINE NITRITES

The prototype of this series, ammonium nitrite, was discovered by J. J. BERZELIUS[15] in 1812 and studied by M. BERTHELOT[16] who found it to be considerably less stable in aqueous solution than in the dry crystalline state, although the solid salt could be detonated by heat or percussion. In contrast to ammonium nitrite, many nitrites of aliphatic or alicyclic amines are stable both in the solid state and in solution. Tetrahydro-α-naphthylamine for example (with the amino group in the reduced ring), gives a nitrite unaffected by boiling with water[17]. Amines of the structure R_2CHNH_2 often give stable, easily isolated nitrites[18] as do several alicyclic amines derived from the terpenes[19]. The nitrites of many simpler aliphatic amines have also been isolated in a more or less pure state and it is recorded that some of them can be sublimed *in vacuo* without decomposition[20].

In 1907 O. WALLACH[19] isolated the first aromatic amine nitrite, that of *m*-xylidine (1,3,4), but it was not until 1932 that aniline nitrite was prepared in a crystalline condition[21]. The method used for its preparation presents some points of interest and will therefore be described.

A concentrated solution of sodium nitrite (1.5 gm in 3 ml water) was placed in a small flask, covered with a layer of pure ether (20 ml) and cooled to about −15°C. At the same time a solution of pure aniline hydrochloride (2 gm in 5 ml water) was prepared and cooled to −8°C, lower temperatures here causing the formation of crystals. The distilled water used for the solutions was boiled and cooled rapidly immediately before use to expel carbon dioxide. The aniline hydrochloride solution was poured rapidly into the nitrite solution with vigorous stirring, care being taken that none of the hydrochloride was left on the walls of the flask. The white precipitate first formed dissolved in the ether on further stirring. The ethereal solution was decanted into a large test tube containing anhydrous sodium sulphate and cooled to −15°C. The extraction with ether was repeated and the combined dry ether solutions evaporated under reduced pressure while still cooling. A mass of white needles remained. On decomposition with alkali the amounts of sodium nitrite and aniline obtained corresponded closely with those calculated for aniline nitrite. The crystalline material was completely soluble in water but precipitation of diazoaminobenzene soon commenced

The solid product underwent spontaneous decomposition when kept at − 6° to − 8°C After one hour all aniline nitrite had completely disappeared, diazoaminobenzene and diazobenzene nitrite being the principal products formed[12]

The nitrites of *p*-toluidine, *p*-phenetidine and *p*-chloroaniline were also isolated in crystalline condition and their decomposition studied both dry and in aqueous and methanol solutions[13] In methanol the nitrite disappeared at a rate corresponding with a second order reaction This fact is significant in the interpretation of the fundamental nitrous acid/amine reaction

One general qualitative conclusion can be drawn from a study of the whole field of amine nitrites, *i e* the nitrites of strongly basic amines are usually more stable in solution than those of weakly basic amines

THE NITROUS ACID/AMINE REACTION

K Arndt[14] and A A Blanchard[15] both studied the decomposition of ammonium nitrite in aqueous solution Although their findings were to some extent in conflict, they agreed that free nitrous acid took part in the reaction Arndt concluded that the reaction was between undissociated ammonium nitrite and nitrous acid, while Blanchard claimed to have shown that the velocity of the reaction was proportional to the concentration of NH_4^+ and NO_2^- ions and was increased by hydrogen ions or free nitrous acid A re-examination of the problem was made by F Abel, H Schmid and J Schafranik[16] who, to avoid the complications resulting from the decomposition of nitrous acid, operated under a positive pressure of nitric oxide They concluded that the reaction involved ammonium ions, nitrite ions and free nitrous acid

In a careful study of the kinetics of the reaction between nitrous acid and methylamine, T W J Taylor was successful in establishing several vital facts[17], although his interpretation of these requires some modification He was able to select experimental conditions which eliminated most of the complications due to the decomposition of nitrous acid and confirmed two observations previously recorded by H von Euler[18], namely

a that with equimolecular proportions of methylamine and nitrous acid in 0 05 N solution at 25°C there was no appreciable disappearance of methylamine,

b that when an additional molecular proportion of nitrous acid was added to the above mixture, the methylamine disappeared at a measurable rate

Taylor observed further

c that the reaction between one mol of methylamine and 2 mol of nitrous acid was retarded by the addition of one mol of sulphuric acid, and

d that the reaction between one mol of methylamine and 2 mol of nitrous acid was accelerated to an equal degree by the addition of one mol of methylammonium chloride or one mol of barium nitrite

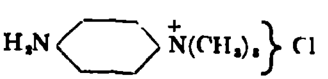
From these data the conclusion was drawn that the reaction was one in which methylammonium ions, nitrite ions and free nitrous acid all took part At the same time, when the reaction was followed quantitatively, it was found that one mol of nitrous acid disappeared for each mol of methylamine and the rate of disappearance of the methylamine corresponded with a bimolecular reaction

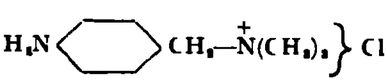
This work was extended to other amines with similar results[19] At that stage the knowledge of the nitrous acid/aliphatic amine reaction had led to the paradox of a bimolecular reaction involving three reactants and the mechanism was not clear[20]

The diazotization reaction with the aromatic amines was studied quite independently of the aliphatic amine reaction A Hantzsch and M Schümann described experiments on the velocity of diazotization and demonstrated that it was a second order reaction[21] Later, Schumann confirmed this conclusion by an independent method[22] For many years it was assumed on the basis of these experiments, that the two reactants were the anilinium ion and nitrous acid Confirmation of the bimolecular nature of the reaction was a result of the work of F Tasilly[23, 24], but no view of its actual mechanism was reached J Boeseken, W F Brandsma and H A J Schoutissen subjected all the earlier work to a critical examination and pointed out several deficiencies in technique leading to inaccurate results They also drew attention to a vital fact ' one will have to take into consideration that the velocity of diazotization may also depend on the basicity of the amine For instance it is not at all out of the question that the reaction takes place exclusively between the free amine and nitrous acid Then this reaction will be quickest with the weakest bases because their salts are hydrolysed to the highest degree[25] ' It should be explained that the objective of this group of workers was not, at first, to correlate basic strength with rate of diazotization, but to establish the influence of substituents on the rate of diazotization as part of a wider study of substitution in the benzene nucleus In a later discussion, Boeseken and Schoutissen favoured the Hantzsch view that the reaction is between anilinium salt and nitrous acid[26]

It is obviously necessary to have a clear demonstration of the relationship, if such exists, between the basic strength of amines and their rate of diazotization. Up to a point, the general experience is that the more weakly basic amines diazotize more quickly than the strongly basic ones. It is also well known that some weakly basic amines are difficult to diazotize and at first sight this appears to run counter to the general rule. However, it should be pointed out that this difficulty to diazotize is associated with the insolubility of the amines concerned rather than with their weakness as bases.

J Reilly and P J Drumm also recorded some experimental results which seem opposed to the general trend[27]. They selected for study a group of amines which they considered they could arrange on general principles in order of the basic strengths of the amino group. The amines were


(*I*)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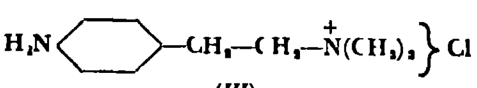

(*III*)

Their classification was based on the known attraction of the $-\overset{+}{N}(CH_3)_3$ group for electrons. They would therefore arrange themselves in increasing basic strength *I* < *II* < *III*. Of the three amines, *III* supposedly the most basic one was the most rapidly diazotized. This was regarded as supporting Hantzsch and Schumann's view of the reaction mechanism.

The irregularities mentioned above may possibly be explained by the simultaneous influence of two factors on the diazotizability of amines, namely, i the reactivity of the hydrogens of the amino group and ii the basic strength of the amino group. Boeseken and his collaborators had noticed this point, but Reilly and Drumm considered the effect of the second factor only. *Table I* indicates the difficulty in arriving at any precise relationship between the velocity of diazotization and the two factors mentioned. It does, however, show clearly that they both have some influence.

Table I Amine Characteristics

Substance	*1*	*2* $\times 10^{-10}$ at 25° C	*3*	*4*
p–*Toluidine*	0.0687	14.8	33.4	96
m–*Xylidine*	0.0886	6.3	—	23.[illegible]
o–*Toluidine*	0.0928	3.3	—	54
Aniline	0.0965	4.6	7.[illegible]	68
m-*Chloraniline*	0.135	0.34	—	2.3
m–*Toluidine*	0.137	5.5		44.5
p-*Chloraniline*	0.153	1.5	1.63	3.4
o–*Chloraniline*	0.483	0.00[illegible]	—	0
m–*Nitraniline*	1.13	0.04	0.041	—

In the first column are given the relative velocities of diazotization of several amines[8]; in the second column are the electrolytic dissociation constants as given in International Critical Tables; in the third and fourth are the relative velocities of benzoylation[18] and of reaction with allyl bromide[14] respectively.

A NEW APPROACH TO THE PROBLEM

During a study of the coupling reactions leading to diazoamino and aminoazo compounds, some remarkable volume changes were observed when the reactions were carried out in methanol solution in a dilatometer. On investigation it became clear that these volume changes occurred during the initial diazotization reaction and very similar changes took place during the nitrosation of secondary amines[28].

When a reaction mixture containing 1 mol methylanilinium chloride, 1 mol sodium nitrite and 0.3 to 0.5 mol of hydrochloric acid in methanol is kept at 8°C, there is a slight decrease in volume during an initiatory period, varying inversely with the amount of hydrochloric acid. Then there is a rapid increase (due to the occurrence of a strongly exothermic reaction) followed by an almost equally rapid decrease to a constant volume[29], *Figure 1*. At first, the explanation of these changes seemed to be that the initiatory period represented the reaction of nitrous acid with methylanilinium ions

$$\overset{+}{N}MePhH_2 + NO \cdot OH \rightarrow NMePhNO + H_2O + \overset{+}{H}$$

While any free methylaniline was present the hydrogen ions liberated in this reaction would immediately take part in the formation of more methylanilinium ions. When, however, no more free methylaniline remained, the hydrogen ions

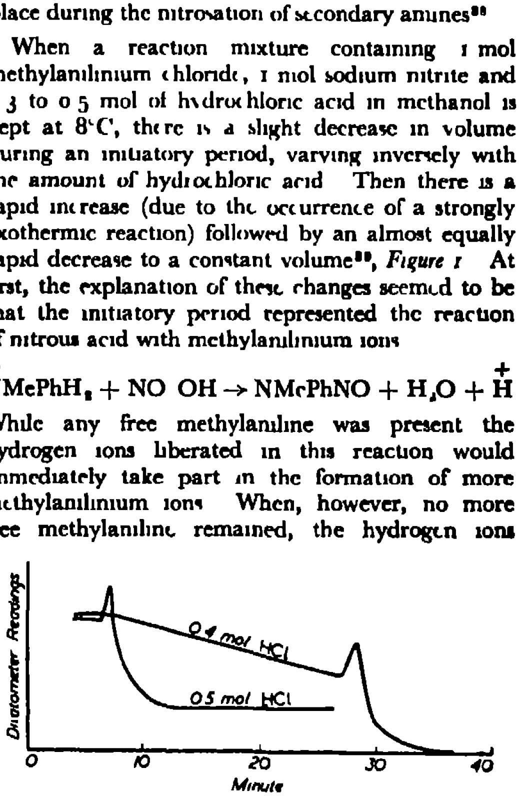


Figure 1 Volume changes during coupling reactions

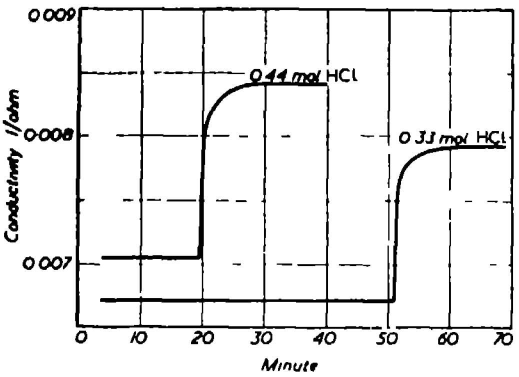


Figure 2 Conductivity changes during coupling reactions

would commence to accumulate and accelerate the main reaction which would proceed rapidly to completion This explanation conforms to the views of Hantzsch and Schumann, but is not the only one which can be offered However, it served the useful purpose of directing attention to the changes in hydrogen ion concentration which might be expected to take place during the reaction In fact, the changes in conductivity when the reaction was allowed to proceed in a suitable conductivity cell were very definite and appeared to furnish convincing support of the mechanism outlined above, *Figure 2*

If the matter had been left at that stage no doubts would have arisen as to the correctness of the conclusions reached When, however, the dilatometric and conductimetric techniques were applied to a larger range of both secondary and primary amines[40], an alternative explanation emerged, which was identical with one suggested by D W ADAMSON and J KENNER[8] for the reaction between the aliphatic amines and nitrous acid It amounted to a classification of this reaction with the group of typical carbonyl/amine reactions which have been so widely studied on account of the chemical interest of such processes as the formation of oximes, hydrazones and anils The nitroso group in nitrous acid might be expected to react in the same way as the same group in numerous organic compounds The analogy between nitroso and carbonyl reactions can be exemplified by reference to the formation of benzalaniline and azobenzene, the first from aniline and benzaldehyde, the latter from aniline and nitrosobenzene The intervention of protons is known to be an essential factor in carbonyl/amine reactions This is in accord with experience of nitroso/amine condensations For example, a solution of equimolecular proportions of aniline and nitrosobenzene in alcohol can be boiled for some time without any perceptible change being observed With the addition of a very small amount of hydrochloric acid, the commencement of the change can be observed almost immediately Similarly, the bubbling of methyl nitrite into an aqueous-alcoholic solution of aniline does not precipitate diazoaminobenzene, but with the addition of two drops of acetic acid there is soon a separation into two layers, one of which solidifies in a few minutes to a mass of diazoaminobenzene crystals

If it is assumed that the reaction between aromatic amines and nitrous acid involves the free amine and undissociated nitrous acid, the behaviour of all classes of amines, aliphatic, alicyclic and aromatic can be correlated[41] The observations of von Euler and of Taylor, already quoted, that methylamine nitrite requires the addition of nitrous acid to bring about its decomposition, can be explained in this way It can be calculated that in a 0 05 N solution of methylamine nitrite probably not more than $2\ 35 \times 10^{-4}$ of the salt is hydrolysed to free base and nitrous acid Further, for all practical purposes, the nitrous acid would be completely dissociated into H^+ and NO_2^- ions There would, however, be some free methylamine If nitrous acid were added, reaction would take place with this methylamine and would continue by upsetting the equilibrium

$$CH_3\overset{+}{N}H_3 \rightleftharpoons CH_3NH_2 + \overset{+}{H}$$

On the other hand, a 0 05 N solution of aniline nitrite would contain about one fifth of the aniline as free amine and a considerable concentration of undissociated nitrous acid Reaction would therefore proceed immediately without the addition of more nitrous acid

The characteristic dilatometer and conductivity curves already mentioned can also be interpreted in the light of this explanation of the reaction In a methanol solution of methylaniline, nitrous acid and hydrochloric acid in the molecular ratio 1 1 0 3 we have the following equilibria operating

$$\begin{array}{lll} & C_6H_5NH_2(CH_3)NO_2 & \rightleftharpoons C_6H_5\overset{+}{N}H_2(CH_3)+\overset{-}{NO_2} \\ a & \quad\upharpoonleft\!\downharpoonright & \\ & C_6H_5NH(CH_3)+HNO_2 & \end{array}$$

$$\begin{array}{lll} & C_6H_5NH_2(CH_3)Cl & \rightleftharpoons C_6H_5\overset{+}{N}H_2(CH_3)+\overset{-}{Cl} \\ b & \quad\upharpoonleft\!\downharpoonright & \\ & C_6H_5NH(CH_3)+HCl & \end{array}$$

$$c\ \ HNO_2+CH_3OH \rightleftharpoons CH_3ONO+H_2O$$

In view of the known ease of esterification of nitrous acid it may be assumed that little free nitrous acid is present in the mixture, but always sufficient to commence the reaction In the early stages, the reactants are furnished from system *a*, the reaction proceeding as it does when no hydrochloric acid has been added The later stages of the reaction call upon system *b* and the hydrogen ion concentration acid Under the more acid conditions, system *c* becomes more labile and liberates nitrous acid more easily Therefore the reaction proceeds rapidly to a conclusion

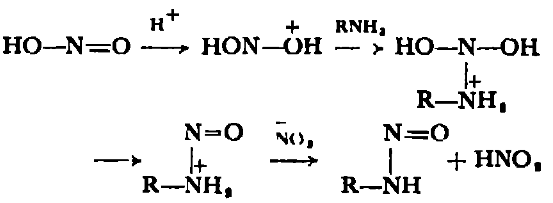
The retarding effect of sulphuric acid on the reaction between methylamine and nitrous acid was attributed by Taylor to the reduction in concentration of nitrite ions If that were so, one would hardly expect the addition of smaller amounts of acid to accelerate the reaction *Table II* relating to the nitrosation of dimethylamine in 0.15 N solution at 5°C shows that such an acceleration does occur when the amount of added acid (hydrochloric or sulphuric) is less than 1 mol The following explanation can be given of the above results Addition of strong acids to a solution of dimethylamine nitrite will increase the concentration of nitrous acid and decrease that of free dimethylamine It would be expected, therefore, that an optimum set of conditions could be reached in which the product $[(CH_3)_2NH][HNO_2]$ is largest and at which the reaction would proceed most rapidly

Table II Nitrosation of Dimethylamine

Mols acid per mol dimethyl amine nitrite	*Nitrite remaining after 3 hours* HCl	*Nitrite remaining after 5 hours* H_2SO_4
0.1	98.0	96.0
0.3	94.7	—
0.5	9[illegible].7	90.7
0.7	94.7	93.4
1.0	98.7	97.3

The view that undissociated nitrous acid and free amine are involved in diazotization and nitrosation is confirmed by the observed effect of conducting the reaction in a solvent of lower dielectric value than water By this means electrolytic dissociation of the amine salt is reduced while its hydrolytic breakdown is favoured C A **KRAUS** and R M **FUOSS**[42] found that tetra*iso*amylammonium nitrate is only feebly ionized in dioxan solution J C **EARL** and N G **HILLS**[43] therefore suggested the study of nitrosation in aqueous dioxan solutions It was found that there is a remarkable acceleration in the nitrosation of dimethylamine with increasing proportions of dioxan up to 67.5 per cent

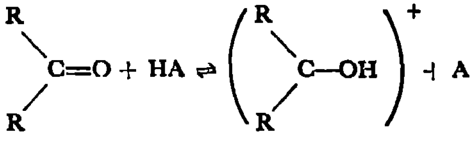
While the evidence in favour of considering the nitrous acid/amine reaction to be similar in mechanism to the carbonyl/amine reaction is strong, there still remains the question of the function of the protons which seem to be necessary for the reaction How can free amine molecules be concerned in the reaction when, at the same time, protons are needed ? Is not this equivalent to assuming that the reacting entity is the ammonium ion and not the free amine ? If one assumes, with Adamson and Kenner[6], that the reaction proceeds



$$HO{-}N{=}O \xrightarrow{H^+} HON{-}\overset{+}{O}H \xrightarrow{RNH_2} HO{-}\underset{R-\overset{+}{N}H_2}{N}{-}OH \longrightarrow \underset{R-\overset{+}{N}H_2}{N{=}O} \xrightarrow{\bar{N}O_2} \underset{R-NH}{N{=}O} + HNO_2$$

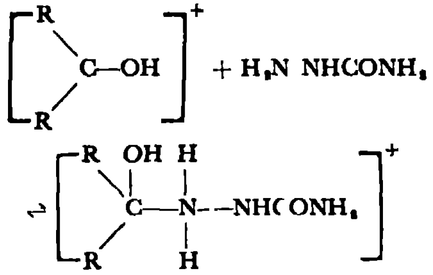
then it is also necessary to assume that conditions must prevail under which it is possible for there to be a distribution of available protons between amine molecules on the one hand and nitrous acid molecules on the other With a strongly basic amine the distribution of protons will be strongly in favour of the amine to the detriment of the nitrous acid, so that the first stage of the above scheme would be hindered With a weakly basic amine, on the other hand, both protons for the first stage of the reaction and free amine molecules for the second would be freely available

The foregoing explanation of the nitrosation reaction emphasizes the capacity of nitrous acid to act as a nitroso compound containing the —NO group It has already been mentioned that there are many analogies between the reactions of the nitroso group and those of the carbonyl group It is, therefore, of interest to compare Adamson and Kenner's explanation of the nitrosation of an amine with L P **HAMMETT**'s views on semicarbazone formation[44] The experimental work of J B **CONANT** and P D **BARTLETT** clearly showed that the rate of formation of semicarbazones depended very definitely on the hydrogen ion concentration of the reaction mixture[45] For example, the optimum *p*H for the formation of acetone semicarbazone was found to be approximately 4.6 Hammett's interpretation of these observations is as follows The first stage in many reactions of the carbonyl group is the addition of a proton

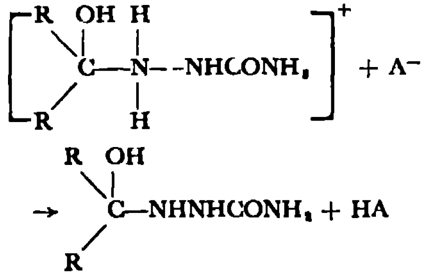


$$R_2C{=}O + HA \rightleftharpoons \left(R_2C{-}OH\right)^+ + A^-$$

In the complex so formed the carbon is even more electrophilic than in the carbonyl compound itself Semicarbazide, being nucleophilic, readily attaches itself to the highly electrophilic carbon to give



and the next stage is the removal of a proton from this complex by the acid anion



Finally, loss of water gives the semicarbazone

ELECTROPHILIC CHARACTER OF NITROSO GROUP

When present as a substituent in an aromatic nucleus, the nitroso group has a strong influence on other substituents Halogens in the *ortho* and *para* positions are rendered extremely reactive and, as is well known, *p*-nitrosodialkylanilines are readily hydrolysed by caustic alkalis to give nitrosophenol and the corresponding dialkylamine This behaviour is similar to, but more pronounced than, that of the nitro group The halogen in *p*-nitrochlorobenzene and in 2,4-dinitrochlorobenzene is also much more reactive than in chlorobenzene, while 2,4-dinitrodimethylaniline is almost quantitatively hydrolysed by boiling with alcoholic alkalis to dimethylamine and 2,4-dinitrophenol We can conclude, therefore, that the nitroso and nitro groups behave similarly, but that the former acts more strongly

There is also a resemblance in behaviour between the nitroso and carbonyl groups Enolization of a $-CH_2CO-$ grouping is paralleled by the nitroso/oximino change, and formation by the formation of azo compounds and so on

All this suggests that these three groups, nitro, carbonyl and nitroso, should be classified together in any attempt to generalize the chemical reactivity of organic compounds The two first are typical cationoid or electrophilic groups and, in general, the nitroso group is to be regarded similarly There is, however, a discordant piece of chemical evidence which cannot be ignored, namely, the apparent *ortho-para* directing influence of the nitroso group when it is attached to an aromatic nucleus Actually, the experimental evidence is not extensive, being practically confined to chlorination and bromination under one set of conditions, namely, in carbon disulphide solution at a low temperature[44] Nitration gives poor yields with many by-products and no other substitution reactions are recorded Moreover, in glacial acetic acid solution bromination does not take place and it has been suggested that, since in this solvent there is little or no association of nitrosobenzene into a double molecule in contrast to its behaviour in carbon disulphide, the *ortho* and *para* derivatives are produced from the bimolecular and not the monomolecular form[47] In the absence of sound experimental evidence to the contrary this explanation cannot be dismissed lightly, although it is possible to give a plausible electronic explanation of the presumed ability of the nitroso group to act as an *ortho-para* directing group[48]

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Honey and its Botanical Sources

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THE shortage of sugar and sweetening materials that took place in many countries as a result of the 1939-45 war was the cause of a general increase of interest in beekeeping and honey production In Great Britain in particular this interest in the honey bee was very marked and was evident among all sections of the community The phenomenal growth and increase in membership of beekeeping associations up and down the country bore testimony to this Beeswax, used in munitions was also in very short supply Another factor which favoured this growth in beekeeping activity was the better understanding of some of the major bee diseases and their prevention and control that has arisen in recent years

The fact that much encouragement was, and still is, given to apiculture from official sources is due to the great value of the honey bee as a pollinator of fruit and various food and seed crops, including the more important clovers In temperate climates the honey bee is of great value as a pollinator in spring when few other insects are about, and is especially valuable for tree fruits

NECTAR AND NECTAR SECRETION

The nectar of flowers has been described as 'the raw material of the honey industry' as indeed it is Not all flowers that produce nectar are of value to the honey bee for the nectar is often too deep seated for her to reach it This applies when the nectar is at the bottom of a long narrow flower tube (the tongue length of the hive bee is some 7–8 mm while that of bumble bees may be 10–12 mm) Nectar is secreted by special organs (nectaries) which vary much with different plants or different groups of plants[1] The actual secretion of nectar is governed by various environmental conditions such as temperature, soil moisture, type of soil, altitude, atmospheric humidity, presence of wind *etc* Conditions for maximum nectar secretion vary a great deal with different plants and a set of conditions favourable for one honey plant may be quite unsuited for free nectar secretion in another Temperature and soil moisture are the all important considerations with most honey plants Some secrete nectar freely at much lower temperatures than others In Britain it is generally considered that willow, *Salix*, and heather, *Calluna*, will secrete nectar at quite low temperatures, appreciably lower than those required for most plants, but further observation and records are needed to confirm this

NATURE OF HONEY

Plant nectar is essentially a dilute solution of sucrose (ordinary or household sugar) generally containing 60–90 per cent of water, together with traces of mineral salts and other substances such as essential or volatile oils, flavourings, gums *etc* These minor constituents become of importance as the water is driven off the nectar in the hive and the nectar converted into honey They are held to be responsible for the aroma and flavour of the honey and account for the well known characteristics of honeys from different floral sources

Vitamins are present in most honeys but only to a small extent, and their value in honey used as human food may be regarded as negligible The presence of vitamins is considered to be due to the pollen grains always present in honey, some pollens being relatively rich in vitamins The protein content of honey is low, too low to be of much food value It varies with different honeys, heather honey and honey contaminated with honey dew having higher protein contents than most other honeys

BOTANICAL SOURCES OF HONEY

The number of species of plants that are visited by the hive bee for nectar is legion There are also species that are visited for pollen only and which do not yield nectar However, in all countries where beekeeping is practised there are certain plants, often few in number, that are responsible for the bulk of the honey crop These are commonly termed the major honey plants The other plants visited by bees throughout the year, which may not be very prevalent or may have a very short flowering season, are often of very great importance to the beekeeper in that they provide food for the bees in the 'off season', enabling them to breed and build up large populations of honey gatherers for the major honey flow when it occurs

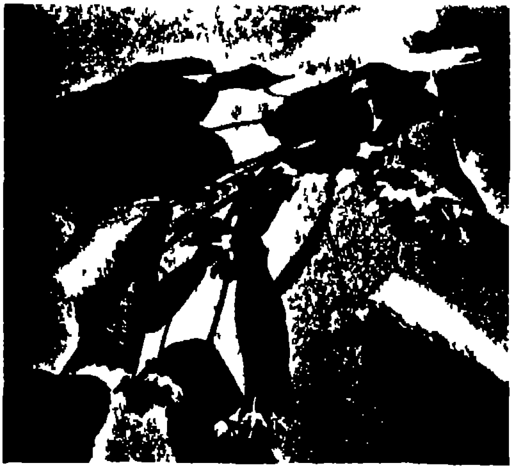

Figure 1 Lime or basswood, Tilia spp, with its sweet smelling blossoms is important for honey in Europe and America

A brief consideration of the major nectar plants in honey producing countries is perhaps best done on a regional or geographical basis, beginning with the British Isles as the country which most readers of this journal are likely to know best

The British Isles—The major honey plants are roughly about a dozen in number and have been listed as follows clover *Trifolium*, lime *Tilia*, heather or ling *Calluna*, tree fruits, sainfoin *Onobrychis sativa*, mustard and other *Brassicas*, hawthorn *Crataegus*, sycamore *Acer pseudoplatanus*, blackberry *Rubus*, willowherb *Epilobium angustifolium*, field beans *Vicia faba* and possibly dandelion *Taraxacum*

The clovers, particularly white clover, *Trifolium repens*, are the most important honey producing plants in the British Isles and at one time were considered to account for about 75 per cent of the country's yearly honey crop The best clover areas for honey production are where the soil has an abundance of lime, as on chalk, the slopes of the Chilterns and Cotswolds being very good Some contend that white clover yields nectar better on hilly slopes than it does on the lowlands[3]

Lime trees (mainly *Tilia vulgaris* and *T platyphyllos*) are important sources of honey to many thousands of urban beekeepers, being fairly common as street and ornamental trees Without the lime, beekeeping would probably not be worth while in many urban areas This probably applies to a large proportion of London's suburbs A serious drawback of the lime is its liability to be attacked by insects secreting honey dew When the honey dew is collected in quantity by bees, as it sometimes is especially in dry summers, it may spoil the quality of otherwise good honey This was a common experience during the hot, dry summer of 1949

The production of heather honey from ling, *Calluna vulgaris* is largely confined to Scotland, although the extensive moors in the north of England are also important while a little is produced on the Devonshire moors True heather honey has several characteristics which distinguish it from other honeys, the most obvious being its jelly-like consistency which prevents it being extracted in the ordinary rotary extractor By many, heather honey is considered the best of all honeys and is much sought after

Fruit blossom (apple, cherry, plum and pear—to place them in their probable order of merit for the beekeeper) constitutes the first potential honey flow of the season for many beekeepers Whether 'surplus' honey, *i e* honey in excess of the bees' requirements, is obtained depends upon the weather and the population or strength of the hive

Sainfoin is a clover-like fodder plant often cultivated in this country, especially where chalk soils abound in the south of England With its deep, penetrating taproot and resistance to dry conditions it is a reliable nectar yielder but the flowering period is short

Mustard and the weed charlock, *Brassica arvensis*, yield a similar type of honey noted for the speed with which it granulates Honey crops are often obtained from them in agricultural districts May or hawthorn is very unreliable as a honey source and the reasons for this are not at present understood

The field bean, also called horse or tick bean, so extensively grown in many parts of the country, especially on heavy land, often yields good crops of honey but the flowering period again is short Plants with long flowering periods which undoubtedly contribute considerably to the total honey crop and which are widespread are the wild blackberry or bramble, willowherb and dandelion

Continental Europe— Much of what has been said regarding the major honey plants of the British Isles applies also to the countries of northern and central Europe, for the same plants occur or are cultivated there The same clovers, tree fruits and crop plants such as mustard and other *Brassicas*, sainfoin, trefoil, *Lotus*, and field beans are commonly cultivated

Buckwheat, *Fagopyrum*, is extensively cultivated as a grain crop in some parts of Europe, notably Russia and France (Brittany), and is important as a honey plant It is essentially a crop for light land Buckwheat flowers do not always secrete nectar freely and are influenced by weather conditions to a marked degree Cool, moist conditions at flowering time are considered most favourable The honey from buckwheat is always dark and of a strong characteristic flavour, not usually appreciated by those unaccustomed to it or used to light mild flavoured honeys

The sweet or Spanish chestnut tree, *Castanea sativa*, extensively grown in parts of Europe for the sake of the nuts is a useful honey source in some seasons, especially in Spain, Italy, southern Switzerland and other parts of central and south Europe False acacia, *Robinia pseudoacacia*, one of the first North American trees to be introduced to Europe and a useful timber tree, is a source of surplus honey in many places in Europe where it occurs in sufficient abundance, *e g* in Italy, Czechoslovakia and the Danubian basin in Rumania In parts of Germany and Switzerland a honey derived from the honey dew of conifers (mainly larch, *Larix decidua*, and spruce, *Abies pectinata*) and known as *Tannehonig* is much in evidence in some seasons and may constitute half the local honey crop

Figure 2 False acacia Robinia pseudoacacia, *one of the first N American trees to be introduced into Europe, may be important for honey where it is freely cultivated or naturalized*

Figure 3 Rosemary is an important nectar source in parts of southern Europe and the main source of the esteemed Narbonne honey of France

In southern Europe and the Mediterranean region fairly pure honeys of somewhat unusual botanical origin are harvested Some of these are from the flowers of fragrant herbs such as lavender, rosemary (Narbonne honey) and thyme and certain districts are famous for their specially flavoured honeys

North America— The United States and Canada are both important honey producers and honey from these countries has been marketed extensively in the United Kingdom in the past In Canada many of the agricultural or field crops and the fruit crops are the same as those of the British Isles and northern Europe Consequently several of the main honey sources are the same Much Canadian honey is derived from clovers, particularly white clover, *Trifolium repens*, and the honey is of the same good quality and fundamentally the same as the white clover honey produced in New Zealand or the British Isles The extensive orchards of apples, cherries and other deciduous fruits afford valuable early bee pasturage as they do in other temperate countries Certain field and wayside weeds are also significant as minor honey sources The fireweed or willowherb, *Epilobium angustifolium*, with its showy pink flowers, is one of the more interesting of these

The botanical sources of honey in the United States are numerous as might well be understood from the size of the country, its varied vegetation, agriculture, topography and climatic conditions The important honey plants of the southern States are entirely different from those of the northern States Over the greater part of the United States cultivated crops of one kind or another are the source of the main honey crop As agriculture has changed in certain States so also has the bee pasturage and the degree of beekeeping activity Sweet clover, *Melilotus*, is an important source Other major sources are white or Dutch clover, *Trifolium repens*, alsike clover, *T hybridum*, alfalfa or lucerne *Medicago sativa*, buckwheat and cotton In certain important honey producing areas the honey crop is derived from wild plants Good accounts of North American honey plants have been given by F C PELLETT[3] and others

Australia and New Zealand—The greater part of the honey produced in Australia, much of which is exported, especially to Great Britain, is derived from Eucalypts Eucalyptus trees are an important and characteristic feature of the vegetation of Australia The genus *Eucalyptus* is a very large one with some 500 species Some are little more than shrubs, while others are among the largest of forest trees They vary much in their nectar secreting properties, also in the quality of the honey they yield In addition to the Eucalypts there are other indigenous trees and shrubs that afford good bee pasture in Australia and may be the source of honey crops in some areas Among these are species of *Tristania* 'brush box', *Melaleuca Leptospermum* tea trees', *Callistemon* 'bottle brush', *Angophora* apples', *Backhousia* 'myrtles' and *Banksia* 'native honeysuckles'

In New Zealand much of the honey that is produced and exported is derived from the introduced clovers in the pastures particularly white clover, *Trifolium repens*, the same clover that accounts for a large part of the honey produced in Europe (including Britain), Canada, the United States and other countries Some of the indigenous trees and shrubs of New Zealand are good nectar yielders and of value to the beekeeper in areas where they are sufficiently prevalent Examples are 'manuka' *Leptospermum scoparium*, 'rata' *Metrosideros robusta* and *M lucida* and 'pohutukawa' *Metrosideros tomentosa*

Southern Africa—In common with many other progressive countries the Union of South Africa and Southern Rhodesia now have a much keener interest in beekeeping than they did before 1939 Up to date methods and equipment are now commonplace The hives used are of the American Langstroth pattern

In spite of a very rich and varied indigenous flora in South Africa the bulk of the honey produced for home use or sale on local markets is derived from cultivated plants or plantation crops of one sort or another The Eucalyptus plantations in all parts of the country, established for timber or fuel in both winter and summer rainfall areas, now afford much useful bee pasturage

In Natal (summer rainfall area) *Eucalyptus saligna* has proved a great favourite with beekeepers in spite of the fact that it is not considered in the front rank among Eucalypts for honey production in Australia It has proved a good nectar yielder in Natal with abundant pollen and a fairly long flowering season

In the Western Cape Province (winter rainfall area) *Eucalyptus viminalis* and *E cladocalyx* are the important honey yielders In this area honey may also be obtained from the multitude of wild heaths *Erica* and heathlike plants that occur

A good deal of the South African honey crop is derived from *citrus*, mainly orange, in the citrus growing districts In the areas where natural forest occurs in the Union, which are restricted and mainly on the east side, a number of tree species may be worked for nectar Together they yield a dark strong honey commonly known as 'bush honey' The same applies in the indigenous forest areas of southern Rhodesia

The Tropics—Although beekeeping with the ordinary hive bee *Apis mellifica* is carried on in many parts of the tropics, either in a primitive native fashion as in most parts of tropical Africa or on modern lines as in parts of the West Indies, honey crops do not, in general, equal those of temperate countries One might imagine tropical conditions would be ideal for honey production but this does not appear to be so Where there is no winter or dormant season there may not be the same inducement for the hive bee to store honey as there is in colder climates

Jamaica has long been an important supplier of honey to the markets of the United Kingdom Much of the honey from Jamaica is considered to be derived from logwood, *Haematoxylon campechianum*

In Cuba honey production is also important and a good account of the nectar sources there has been given by G S ORDETX[4] Some of these are indigenous plants that do not occur or are not important in other countries The red and the white 'aguinaldo' or bell flower (*Ipomoea*), common climbing plants like 'morning glory' (*Convolvulus*) are considered to produce over one third of Cuba's total honey crop, yielding a delicious pearl-white honey. Another decorative climber regarded as a first class nectar yielder is the coral creeper *Antigonon leptopus*.

In the Asiatic tropics apiculture has not been developed extensively or on modern lines. Well known crop or economic plants of the eastern tropics known to be good sources of nectar include the coconut and other palms, cotton, coffee, sesamum, pigeon pea *Cajanus*, safflower *Carthamus*, mango, banana, tamarind, rose-apple *Eugenia*, the lime and other citrus fruits.

NEED FOR MORE KNOWLEDGE

Although comprehensive accounts have been given of the honey-bee pasturage of some countries (notably the United States, Great Britain, parts of Europe and Australia, Cuba *etc*) little appears to be known or recorded regarding the floral sources of honey in many of the countries where beekeeping is carried on.

In many parts of Asia, including both Near and Far East, very little seems to have been recorded on the plants of value to the hive bee. The same applies to many tropical American countries and to tropical Africa, in spite of the fact that East Africa and Abyssinia are important commercial sources of beeswax. It is to be hoped that these gaps in our knowledge of the world's honey sources or honey bee pasturage will, in time, be filled.

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[2] Manley, R. O. B. *Honey Farming*. London, 1946.
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Cawthron Institute

Sir THEODORE RIGG, K.B.E., M.A., D.Sc.

Director of the Cawthron Institute, Nelson, New Zealand

THE Cawthron Institute owes its origin to the munificence of THOMAS CAWTHRON, who left practically the whole of his fortune for the establishment and conduct of a scientific institute and museum.

The original trustees, appointed under the will of Cawthron, decided, on the recommendation of a Scientific Advisory Committee, that the major activity of the Institute should be research in the interests of New Zealand agriculture with reference to problems of both farmers and orchardists. The proposals of the trustees were approved by the Supreme Court and early in 1920 the nucleus staff under the Directorship of the late Sir THOMAS EASTERFIELD was appointed and work was commenced.

Three main departments of scientific research were established in 1920 and these were maintained with but little change until the close of 1941, when a biochemical department was formed to handle plant and animal nutritional problems more effectively. The principal work of the four scientific departments is connected with *1* soil and general agricultural problems, *2* plant chemistry and mineral deficiency problems of stock, *3* insect problems of farm, orchard, timber and the biological control of noxious weeds, *4* fungus disease problems of fruit, hops, tobacco, and market garden crops. A technical museum, having special reference to the primary industries of Nelson and the natural history section of museum work, forms an integral part of the Institute and provides suitable facilities for the presentation of the work of the research departments to the general public.

Since the inception of the Institute seven additional bequests and grants have been received. In recent years the Minister of Scientific and Industrial Research has given financial assistance for soil, mineral deficiency, tobacco, fruit and entomological investigations. In several branches of research work the staff of the Institute collaborate with officers of the Department of Scientific and Industrial Research. Entomological, tobacco and hop research at Nelson are conducted on a cooperative basis, both Cawthron and Government officers sharing in the research programme.

WORK OF THE INSTITUTE

The Nelson district in which the Cawthron Institute is located has a climate which favours horticulture, and it is in this branch of agriculture that marked development has taken place in recent years. The whole of the tobacco and hop industries of New Zealand are located here; in addition Nelson has a very important section of the apple industry together with considerable acreages of small fruits, tomatoes and market garden crops

Arable, dairy and sheep farming are all represented in the agriculture of Nelson, and problems connected with these branches of agriculture in addition to horticultural crops have been investigated by the Institute

One of the interesting features of the district is its diverse geology In addition to several well defined sedimentary formations, ultra-basic rocks of serpentine, basic rocks of melaphyre and acidic granites, outcrop in the district and exert a pronounced effect on the properties of the different soils The study of the soils of the Nelson district and their uses for different crops has given information of great value not only to local agriculture but to other areas in New Zealand where similar soils occur Striking deficiencies of lime, phosphate, and potash have been found in several soils, while minor element deficiencies of cobalt, boron and magnesium have been identified on particular soils and studied intensively

Although the work of the Cawthron Institute is not confined to the Nelson district a great deal of its work is associated with the soils and special crops of Nelson The work of the entomological department at the Cawthron Institute, however, has a more general application in that the parasitic control of insect pests and the biological control of weeds, as a rule, apply in equal measure to agriculture throughout the whole of New Zealand

In several aspects of soil, plant, and insect research the Cawthron Institute has gained special distinction for the initiation and development of work of major importance to New Zealand agriculture This is particularly true in connection with the work carried out by the Institute in soil surveys, trace element deficiency, the parasitic control of insect pests, and the biological control of noxious weeds

SOIL SURVEYS

One of the important investigations commenced in the inaugural year of the Cawthron Institute was a reconnaissance soil survey of Waimea County, Nelson This constituted the first systematic soil survey conducted in New Zealand which gave due recognition to the important part played by both geological origin and texture in soil properties Although modern methods of soil classification have necessarily entailed a revision of the soil groups identified in these early surveys, the units set out on the soil maps have required little alteration and have proved invaluable in the conduct of investigations relating to animal health, plant nutrition and the manuring of crops

Among the soils of the Waimea County which have proved of special interest to Nelson, and indeed to the whole of New Zealand, may be mentioned Moutere loams and Kaiteriteri loams The Moutere soils have furnished spectacular deficiencies of lime, phosphate, nitrogen, potash, boron and magnesium, several of which have seriously limited both yield and quality of crops, particularly of apples grown on these soils The Kaiteriteri group, derived from granite, has marked deficiencies of cobalt, boron, and magnesium In no part of New Zealand are the characteristic properties of the soils so divergent and the value of soil surveys in the development of agriculture so clearly apparent

The success achieved by the Institute in soil survey work in Nelson led to the establishment of a Soil Survey Division by the Department of Scientific and Industrial Research and the initiation of a reconnaissance survey of the volcanic ash soils of the central North Island territory of New Zealand The Cawthron Institute was intimately associated with this and other surveys which were carried out in Taranaki, the Waikato, North Auckland, Hawke's Bay, and other parts of New Zealand The reconnaissance survey of the volcanic ash soils proved of very great value as some of the soils were associated with stock ailment When, as a result of other investigations, the cause of ' bush sickness ' was identified as cobalt deficiency, the survey of the volcanic ash soils made possible the immediate application of this discovery to practically the whole of the affected country in the North Island

In more recent years soil survey work at the Institute has been concentrated on the detailed mapping of the alluvial soils of Nelson for the expansion of the flue cured tobacco industry Quality in flue cured tobacco is dependent on the selection of light textured soils and the judicious use of fertilizers whereby a satisfactory yield is obtained without lowering the quality of the cured leaf Some 50,000 acres (20,250 hectares) of the alluvial soils of the Waimea County have been carefully examined and soil maps on a scale of 4 in to 1 mile (6 4 mm to 1 km) prepared From these detailed maps the soils have been grouped into six categories, four of which are regarded as good to satisfactory for use in the culture of flue cured tobacco As a result of this and parallel work by the Cawthron Institute and the Department of Scientific and Industrial Research, the flue cured tobacco industry in Nelson has shown striking development during the past ten years The acreage under tobacco has been more than doubled while the yield per acre has likewise been increased at least a hundred per cent without detriment to the quality of the tobacco

Another aspect of the soil work of great importance to agriculture in Waimea County is that connected with land utilization and soil conservation. Maps have been prepared showing the present use of the land and areas of poor hill country which should be retired from agriculture with a view to the better control of rivers and the prevention of soil erosion and flooding of the valuable alluvial soils of the County.

TRACE ELEMENT INVESTIGATIONS

The Cawthron Institute has played an important part in the identification of trace element deficiency affecting both animals and plants in different parts of New Zealand. The investigations of the Institute have comprised studies of cobalt deficiency in the granite soils of Nelson Province and the loess soils of Southland, boron deficiency on two soil types in the Nelson district and on several soils in Central Otago, and magnesium deficiency of apples and tobacco on the granite and Moutere Hills soils of Nelson.

Cobalt deficiency.—Studies of ‘ bush sickness ’ in sheep on the granite soils of Glenhope were commenced in 1928, and of lamb ailment in Southland in 1934. Evidence was slowly accumulated which ruled out a theory of iron deficiency as the cause of these stock ailments and suggested another element contained in certain iron ores and soil ‘ licks ’ which had proved beneficial in the treatment of stock ailment.

Aided by the announcement from Australia that cobalt was an element of nutritional importance to stock, chemists at the Cawthron Institute quickly showed that cobalt overcame stock ailments at Glenhope and Southland, and that there was an actual deficiency of cobalt in the soils, pastures and organs of affected animals. The work carried out by the Cawthron Institute on cobalt ‘ licks ’ and the use of cobaltized fertilizers has had a wide application not only in New Zealand but in other countries where cobalt deficiency has been identified.

As a result of the investigations carried out by the Department of Agriculture in the North Island and by the Cawthron Institute in the South Island, it can be said that cobalt deficiency in New Zealand has been overcome, the production of fat lambs and successful dairying has become possible over hundreds of thousands of acres which were formerly seriously affected by stock ailment or under suspicion.

Boron deficiency.—Similar work has been carried out by the Institute in regard to the incidence of boron deficiency in apples, apricots, plums and grapes on certain fruit soils in Nelson and Central Otago. Surveys of the boron content of soils and fruit have been carried out in all fruit growing districts of New Zealand and methods for overcoming a deficiency have been studied. The investigations have shown that boron deficiency in fruit trees can be controlled by the use of ½ lb (0.2 kg) of borax per tree or by the use of borax sprays at 0.1 per cent strength. One of the interesting features of the experiments on apples was the adverse effect on keeping quality when borax was used in excessive amount.

Another aspect of boron deficiency investigated by the Institute on the soils of the Waimea County is boron deficiency of tobacco brought about by the use of lime in too large applications on the sandy soils associated with the culture of this crop. The arrest of the growing point and the pronounced dwarfing of the tobacco plants are characteristic features of boron deficiency resulting from the injudicious use of lime on these soils.

Still another case of boron deficiency has recently been identified on Nelson soils. Raspberries which are grown extensively on soils derived from granite and from the ‘ Moutere gravels ’ have been affected in certain seasons with marked ‘ die back ’ of the canes. This trouble, which formerly was considered to result from root diseases, has now been shown to be caused by a deficiency of boron. The soils contain less than 0.25 ppm soluble boron and the leaves of affected raspberry bushes contain greatly reduced amounts of the element. The effect of boron deficiency on raspberry canes is the arrest and early death of all the fruiting spurs on the canes. Borax applications at the rate of 40 lb/acre (22 kg/ha) have given a satisfactory control of ‘ die back ’ caused by boron deficiency.

Magnesium deficiency.—Studies of fruit trees in the Nelson district have shown the presence of magnesium deficiency on the Moutere Hills type of soil. Premature defoliation of trees had been noticed in certain apple manurial experiments of the Institute. Injection of different elements into the limbs of affected trees showed that magnesium salts were highly beneficial in controlling defoliation. Analyses of the leaves of affected trees showed a high deficiency of magnesium. The identification of magnesium deficiency in apples under commercial conditions of culture was of considerable interest. The Nelson work paralleled similar investigations carried out by Long Ashton workers in England and suggested the possibility of a fairly common occurrence of magnesium deficiency in horticultural crops on soils naturally low in bases, particularly where excessive amounts of potassic manures have been used. An interesting feature of the Nelson experiments on the control of magnesium deficiency in apple trees has been the success achieved with ground dolomite in restoring affected trees. This magnesium compound used at the rate of 12 lb (5 4 kg) per tree has given more permanent benefit than the use of the corresponding quantity of magnesium sulphate

Zinc deficiency— Still another trace element deficiency on the Moutere type of soil is being investigated at the present time This is a suspected case of zinc deficiency in fruit trees in the Tasman locality While the effect of zinc sprays and the zinc content of leaves from affected trees support a theory of zinc deficiency as the cause of ' die back ' in cherries, no evidence has been obtained so far that apple trees on this soil type are affected by a deficiency of this element

PARASITIC CONTROL OF INSECT PESTS

Orchardists in New Zealand will always remember the spectacular success achieved by the Cawthron Institute through the introduction of *Aphelinus mali* parasite for the control of woolly aphis which, for many years prior to the introduction of the parasite, had been one of the serious pests of New Zealand apple orchards

The parasite, obtained through Dr HOWARD, U S A , established freely in New Zealand and very quickly brought about a great reduction in woolly aphis, thereby saving many thousands of pounds in the cost of oil sprays

Similar work has been carried out by the Institute in the introduction of the parasite *Habrolepis dalmani* for the control of ' golden oak scale ' Liberations of the parasite were made at Nelson, Christchurch and New Plymouth The parasite was an outstanding success and gave an effective control of ' golden oak scale '

A more recent introduction by the entomologists at the Institute has been that of *Rhyssa persuasoria*, for the control of the horntail borer which attacks pine plantations The parasite has been liberated at several centres in the South Island of New Zealand and has multiplied rapidly There is every indication that the parasite will prove valuable in the control of the horntail borer

BIOLOGICAL CONTROL OF NOXIOUS WEEDS

Although several insects have been introduced with a view to the control of noxious weeds in New Zealand, success has been somewhat limited The Cinnabar moth and the ragwort seed fly were both introduced for the control of ragwort but so far have not been successful under field conditions in the control of this weed

The Chilean saw fly was likewise introduced in an attempt to control piripiri, but although quite effective under laboratory conditions this insect so far has not been successful under field conditions

The gorse seed weevil, *Apion ulicis*, however, has established freely at all points where liberations have been made Examinations of gorse pods show that the weevil is exerting a marked effect on gorse seed production and should eventually be an important factor in controlling the spread of the plant

The recent introduction of the European beetle *Chrysolina hyperici*, obtained through the good offices of C S I R , Australia, for the control of St John's wort, has proved an outstanding success and where liberated in the Awatere Valley, Marlborough and in Central Otago has cleared hundreds of acres of St John's wort infested country

The establishment of the Entomology Division of the Department of Scientific and Industrial Research at the Cawthron Institute under the direction of Dr D MILLER, Chief Entomologist to the Institute, has greatly strengthened entomological research at the Institute The work carried out by the Government entomologists on the parasitic control of the white butterfly and the diamond back moth has been very successful and has resulted in immense savings to farmers throughout New Zealand

PLANT PATHOLOGY

The horticultural crops of Nelson provide great scope for Cawthron mycologists Their services have been in constant demand by orchardists, tobacco growers and market gardeners for the identification of diseases and for advice concerning their control

Outstanding work has been carried out by mycologists in the study of ' black spot ' of apples, ' brown rot ' of stone fruit, diseases of small fruits and tomatoes In recent years very detailed studies have been made of tobacco mosaic and the factors which operate in its dissemination in the tobacco gardens The importance of the seedling bed stage in mosaic transmission has been established and the necessity for the greatest care in handling plants to avoid infection has been stressed Several tobacco diseases, new to the Nelson district, have been identified by the mycologists Among these may be mentioned ' angular leaf spot ', ' verticillium wilt ' and ' black root rot '

A series of investigations have been carried out in cooperation with officers of the Department of Scientific and Industrial Research, in regard to the control of both ' black root rot ' and ' verticillium wilt ' The importance of steam sterilization or disinfection of the seedling beds with chloropicrin in the control of ' black root rot ' has been clearly shown in the experiments Similar work in regard to the control of ' verticillium wilt ' has shown the value of chloropicrin treatment, but the cost of the chemical at present rules out the possibility of its use under field conditions of culture

More recently investigations have been commenced concerning the identification and control of certain root diseases of hops It has been found that the most serious root disease is ' black root rot " *Phytophthora* sp but canker (*Gibberella* sp, *Fusarium* sp) is also present The early identification of diseases and the application of suitable control measures have been of great importance in the successful development of horticulture in the Nelson district

In this brief review of the work of the Institute it has been possible to describe only the more important activities of the Institute During the thirty years of work at Nelson a great variety of work has been successfully handled and no less than 500 scientific papers have been published by members of the staff

The success of the Institute has not depended solely on the research carried out at Nelson Of almost equal importance has been the great influence, particularly in the early years of its work, on farmers and citizens throughout New Zealand The success of the Institute stimulated agricultural research in governmental and farming circles and assisted greatly in a correct appreciation of research by the general public of New Zealand

Miscellaneous Notes

ROYAL SOCIETY LECTURES 1950

THE Croonian Lecture will be delivered on 15 June by Professor F M BURNET, F R S, Director of the Walter and Eliza Hall Institute, Melbourne, Australia

The Bakerian Lecture will be delivered on 4 May by Professor P W BRIDGMAN, FOR MEM R S, Lyman Laboratory of Physics, Harvard University

The Ferrier Lecture will be delivered on 29 June by Professor J Z YOUNG F R S, Professor of Anatomy, University College, London

The Wilkins Lecture will be delivered on 14 December by Professor F J COLE, F R S, Emeritus Professor of Zoology University of Reading

The first Leeuwenhoeck Lecture will be delivered on 9 November by Sir PAUL FILDES, F R S

UNIVERSITY APPOINTMENTS

Alexandria, Farouk I University— Professor D THODAY has been appointed Professor of Plant Physiology

Battersea Polytechnic— The new Head of the Department of Chemistry is L W DERRY who succeeds Dr W A NAISH

Belfast, Queen's University— Dr R A R GRESSON has been appointed Professor of Zoology

Cardiff— Dr J G C ANDERSON is the new occupant of the Chair of Geology

Durham, King's College, Newcastle— Dr A A HARPER has been appointed as the new Professor of Physiology

Leeds— Dr H C VERSEY has been appointed Reader in Applied Geology

Manchester— Professor P M S BLACKETT, F R S, has been appointed a Pro-Vice-Chancellor

M J LIGHTHILL has been promoted to be Reader in Mathematics

North Staffordshire University College - Among the first appointments are the following as full time Professors I N SNEDDON (Mathematics), Dr H D SPRINGALL (Chemistry), S H BEAVER (Geography), B R WILLIAMS (Economics), Dr V A VICK (Physics), Dr A R GEMMELL (Biology)

Otago New Zealand— Professor N E ODELL has been appointed Professor of Geology

RESEARCH APPOINTMENTS

British Iron and Steel Research Association— Dr J PEARSON has been appointed Head of the Chemistry Department in succession to Dr F D RICHARDSON He has been Head of the Chemistry Section of the B I S R A Laboratories at Sketty Hall, Swansea

British Railways— E MORGAN has been appointed Senior Research Engineer, London Midland Region, as from 1 February 1950 He first joined the Research Department at Euston in 1933

Wool Industries Research Association— The Council has selected Dr A B D CASSIE to fill the vacant position of Director of Research as from 1 January 1950 Dr Cassie has for some years been Head of the Physics Department and during the last two years has been Deputy Director of Research

AWARDS

Institution of Electrical Engineers— The Faraday Medal has been awarded to Sir JAMES CHADWICK, F R S, for his contributions to science generally, and in particular for his distinguished work in nuclear physics

Institute of Fuel— The Melchett Medal for 1950 has been awarded to Professor R J SARJANT, Professor of Fuel Technology, University of Sheffield

RESEARCH ASSOCIATIONS

British Non-ferrous Metals Research Association— The following elections are announced

Chairman of Council Lieut-Col the Hon R M PRESTON, D S O

Vice-Chairman and Hon Treasurer F C BRABY, M C

Chairman of Research Board Dr M COOK

British Shipbuilding Research Association— The hull of the Clyde paddle steamer ' Lucy Ashton ' has been purchased Investigations of technical problems by means of model experiments will be followed up by full scale tests Possible experiments include the determination of the resistance of the hull over a range of speeds

BRITISH COUNCIL

Sir HENRY DALE, F R S, has been elected President of the British Council in succession to Lord RIVERDALE who has resigned

COLONIAL RESEARCH SERVICE

This service has been formed retrospectively to gather the scattered research workers of the British Colonial Empire Mobility of research personnel will be the keynote Service is pensionable, on the same basic salary scales as for the United Kingdom Scientific Civil Service, except for the medical and veterinary research officers who will enjoy substantially increased remuneration Full details are obtainable from the Colonial Office, Sanctuary Buildings, Great Smith Street, S W 1

COMING EVENTS

Convention of Electric Railway Traction, London, 20 23 March

Conference on Theory of Photographic Processes, Bristol, 28–31 March

Fourth National Plastics Exposition, Chicago, 28–31 March

Faraday Society Biophysics and Colloids Committee Discussion on Physicochemical Properties and Behaviour of Nucleic Acids, London, 12 May

CORRECTION

In the February issue of *Research*, p 66, Formula *XIV* should contain a double bond in the side chain, as will be seen from valency considerations There should be no double bond in Formula *XV*

New Books

Advanced Treatise on Physical Chemistry, I Fundamental Principles , Properties of Gases

J R PARTINGTON

(*xliii + 943 pp, illus, 9¾ in by 6 in*)

London Longmans, Green and Co Ltd, 1949 80s net

THE task involved in writing a comprehensive textbook of physical chemistry has increased enormously since OSTWALD and NERNST wrote their classical treatises of general and theoretical chemistry There have not been lacking those who have faced single handed the ever increasing burden, among whom W C M LEWIS and K JELLINEK (1928) may be mentioned, and of whom Professor PARTINGTON is the latest exemplar The cooperative writing of senior textbooks has been in favour in recent years, and by this procedure the reader is brought up to the limits of growing science more effectively than by the perusal of a book written by a single individual There is, however, usually a lack of evenness of presentation and uniformity of nomenclature in cooperative textbooks which reduces their value as works of reference

Professor Partington has outlined his plans and objectives in a very provocative preface, which itself makes interesting reading He states that his object has been to present a proper balance between theory and experiment, and he is critical of books which only refer to work which is in line with present day theories He has a special affection for the errant fact that refuses to be dragooned into an ordered array He is endeavouring ' to give information to those who are in search of it, and not to train students ' He has in mind three or four volumes, of which only the first volume is in print The first five sections of the present volume relate to fundamental principles Thus, there is a comprehensive mathematical introduction beginning with the elements of the calculus and ending with differential equations, and there are sections on thermodynamics, kinetic theory of gases, statistical mechanics, quantum theory and wave mechanics Temperature and the properties of gases are dealt with in the last two sections, in which great emphasis is laid on experimental technique

With only one volume in print it is not easy to discern the author's plan for the whole of the treatise

It is inferred from the way he has grouped the fundamental sections at the beginning of the first volume that he plans to present the more coherent parts of physicochemical theory in broad masses, and then to proceed to link experiment with theory in the more applied sections This has the disadvantage that the theoretical sections have been so divorced from experiment that the theory in places appears to be unnecessarily arbitrary Thus, wave mechanics is developed without reference to spectra, and thermodynamics elaborated with the minimum discussion of experiments It has also led—although this is not inherent in his plan—to the somewhat haphazard introduction of principles not relevant to the main theoretical topics into the applied sections In this way magnetic susceptibility makes its appearance in the low temperature section In addition it has led to duplication the flow of gases through narrow tubes is dealt with both under 'kinetic theory' and under 'properties of gases' Blemishes of this character are perhaps unavoidable in any plan which attempts to classify such a large mass of interrelated material

The author's task has been lightened by the fact that he has previously written textbooks on thermodynamics and statistical mechanics, mathematics for chemists, and the history of science, which material he has been able to incorporate into the book One of the good features of the book is to be found in the interesting historical introductions, which lead naturally into the main body of doctrine The historical approach lends a good deal of interest to the book

In a textbook of this magnitude there are bound to be many points which the experts would have elaborated with greater perfection The mathematics section will undoubtedly prove very useful to those who wish to find in one source all the mathematics they need The more difficult sections are, however, not always sufficiently developed to be easily comprehended by the type of reader that the author has in mind. This in the main is due to the necessity for fuller explanation, notably in the treatment of Fourier's integral, p 111, and the wave equation, p 101. His treatment of the Gibbs-Duhem equation on p 173 is not sufficiently clear, and there is an error in equation 8 In the treatment of thermodynamics there are elements of illogicality, especially the treatment in section 33 of $F = U - TS$ Whilst there is a full discussion of viscosity, it is not easy to find values of mean free paths and collision diameters. The data on these properties given on pp 852 and 857 are not referred to in the index These points of criticism, however, relate to quite small sections of the material of the book, which is otherwise very valuable as a work of reference.

The author claims that his book will be of value to laboratory workers and to chemists and engineers engaged in large scale operations In the reviewer's opinion he has succeeded in this aim, and has provided a very readable book which at the same time is a mine of experimental data It does provide a first book of reference to the practical man, both on the mathematics and theory of physical chemistry and on experimental methods If there are any obscurities—and there are a number—further reference to more specialized textbooks and dictionaries will help to fill the gaps There are extensive summaries of literature abbreviations, symbols, and fundamental physical constants, and the nomenclature is consistent throughout the book The book is printed on good paper and well illustrated

W E GARNER

Photoelectricity and its Application

V K ZWORYKIN and E G RAMBERG

(xii+494 pp, 987 illus, 9 in by 6 in)

New York John Wiley and Sons, Inc , 1949 $7 50
London , Chapman and Hall Ltd, 1949 45s net

THE authors state clearly in their introduction that the book stresses applications of photoelectricity and they relegate all mathematical treatment to footnotes The text is intended for students and engineers, although probably few of the former will care to purchase it and indeed would probably benefit much less from it than the latter, who should find much stimulating matter in it Despite a personal preference for more fundamental treatment on the lines of the excellent short summary of electron lenses in Chapter 9 relating to image tubes, and for less on miscellaneous applications such as the Type Z Helmet Binocular (p 417), the book must be judged as a manual of applied photoelectricity

Being acknowledged leaders in this field, the authors have clearly and successfully attempted a comprehensive review covering as many applications of photoelectric devices as possible Out of 20 chapters, the first three deal with fundamentals, the next three with techniques (preparation of photoelectric surfaces, vacuum technique, seals *etc*) and the following five with the properties of photoelectric devices such as vacuum, gas-filled and multiplier phototubes, image tubes, and photoconductive and photovoltaic cells The remaining nine chapters, with the exception of chapters on circuits and the measurement of small photocurrents, deal with applications including as examples sound reproduction television, picture transmission and light beam signalling Attractive features of the book are the generous bibliographies at the end of each chapter.

The illustrations are lavish, and the printing and binding of the highest quality

J D CRAGGS

Le Calcul Mécanique

R TATON

(*126 pp, 42 illus, 7 in by 4½ in*)

Paris Presses Universitaires de France, 1949 *c Fr* 150 0
London H K Lewis and Co Ltd, 1949 *c* 4*s* 6*d*

THIS little volume contains a wealth of information on the history and development of calculating machines The subject is treated roughly chronologically and, after a few introductory remarks on such early aids to calculation as the abacus, the author works steadily from the first machines of PASCAL and LEIBNIZ to some of the latest electronic calculators

The author is concerned both with the development of the various mechanisms used in calculating machines and with the uses to which the machines can be put The engineering aspect is discussed with the aid of a plentiful supply of sketches and associated descriptions which are quite detailed The uses of the machines can of necessity be dealt with only in very general terms and the author rightly concentrates on how the machines carry out the various elementary operations into which most problems can be broken down

The absence of any reference to many of the most popular modern machines may surprise the reader but is explained by the author's historical approach , he is concerned usually with describing the first machine to embody a new feature rather than improved models displaying no fundamentally new features More serious is the omission from the chapter on scientific work of any reference to the use in this field of the machines (desk, accounting or punched card) already described in earlier chapters The paragraph on p 116 touching on the use of finite differences is also extremely misleading

When so much is packed into such small compass it seems ungracious to complain of omissions, however, and the author is to be congratulated on writing a book which even the poorest linguist can find so readable

E T GOODWIN

The Physics of Rubber Elasticity

L R G TRELOAR

(*viii+256 pp; illus, 8½ in by 5½ in*)

London Oxford University Press, 1949 21*s* net

THIS monograph gives a survey on rubber elasticity, including a description of the main experimental facts and a clear presentation of the theoretical considerations in a mathematical, though not too mathematical, language

The introduction contains a short presentation of the chemical characteristics of rubber-like substances and a description of their main physical, in particular thermodynamic, properties Simultaneously with the enumeration and description of these properties, kinetic and statistical considerations are introduced A presentation of the quantitative statistical theory of rubber elasticity, its criticism and refinements are contained in subsequent sections They form the main part of the book, the presentation of experimental facts alternating continuously with theoretical explanations and considerations The main subjects treated are the stress/strain relationships in the region of small, as well as very large, strains , the relationships between stress-birefringence and mechanical properties , crystallization, and the relaxation and flow phenomena

It is worth mentioning that the author took great care to give a correct historical account of experimental and theoretical developments A small point to add would be that it was E WÖHLISCH in 1926 who gave the first definite statement that the retractive force in extended rubber is a kinetic phenomenon , an idea which was later taken over by the other authors mentioned in the monograph

It is fortunate that the present book is written by an author who himself has taken an active part both in the theoretical and experimental development of this field and is therefore familiar with both aspects , an essential condition for a successful treatment of the subject The monograph can be warmly recommended both to beginners and to advanced workers on rubber and rubber-like substances.

W KUHN

Leitfähigkeit und Leitungsmechanismus fester Stoffe

E JUSTI

(*xii+348 pp, 220 illus, 9 in by 6 in*)

Göttingen Vandenhoeck und Ruprecht, 1948 *DM* 17 50
London H K Lewis and Co Ltd, 30*s* 8*d*

THIS book represents an expanded version of a series of lectures given by the author to an audience of electrical engineers The table of contents includes three chapters on the conduction of electricity in metals, and further chapters on thermoelectricity, electrical contacts and crystal rectifiers, semiconductors, superconductivity, photoconductivity and ionic conduction

The book performs a useful function in collecting together a large amount of experimental material and in providing a bibliography which appears to be fairly comprehensive and up to date Unfortunately, however, the author, who seems to have pursued a variety of conflicting aims, has interspersed the text with elaborate descriptions of demonstration experiments and with an uncritical recital of theories, many of which possess historical interest at best, combined with attempts at elementary explanations of intricate topics such as the quantum mechanical theory of the resistance mechanism in metals The result is somewhat confusing, and it is not clear whether the intention has been to give a general survey of the subject suitable for the non-specialist, or to describe the present position in detail to the expert and to indicate where further research is most needed. The first of these aims has certainly not been realized since the book is too heavily loaded with detail and the theoretical ideas are too little coordinated to enable a clear picture of the fundamental concepts to emerge The book cannot, therefore, be recommended to the general reader, but, if it is read with caution and if parts of it are disregarded, its account of recent experimental work will be of considerable interest to those actually working on aspects of the subject Much of the work described was done in Germany during the war and is not yet generally known in this country

It must be added that the book is poorly produced and abounds with minor errors and misprints, but this may perhaps be blamed on present production difficulties in Germany

E H SONDHEIMER

Atmospheric Turbulence

O G SUTTON

(*viii+107 pp, 4 illus, 6¾ in by 4¼ in*)

London Methuen and Co Ltd, 1949 6*s* net

Oscillations of the Earth's Atmosphere

M V WILKES

(*ix+76 pp, 29 illus, 9 tables, 8½ in by 5½ in*)

Cambridge University Press, 1949 12*s* 6*d* net

THESE two little books, the first textbooks available in this country on their respective subjects, make a welcome addition to the library of the meteorologist or the mathematical physicist interested in meteorological subjects They bring together in proper sequence and ordered form the results of a wide but highly specialized range of researches, hitherto scattered, about the proceedings and journals of the scientific societies

The first book opens with an account of viscosity and turbulence on the laboratory scale, and passes on to a chapter on the meteorology of the lower atmosphere, questions of lapse rate, profiles of wind, temperature and humidity near the ground and so on. This chapter indicates at once the limitations which the author has been obliged to impose on the treatment of his subject in order to compress the book to a total of just over 100 pages The book is, in fact, essentially the mathematical physics of turbulence and diffusion in air in the region for which adequate data exist, namely within a few hundred feet of the ground Later chapters deal with mixing length, statistical theories of turbulence and diffusion in the atmosphere, aspects which have important applications in the military and industrial spheres and in public health

The second book is mainly mathematical The writer gives a clear account of the lunar and solar air tides The existence of the lunar tide and its main features have been established in major researches by CHAPMAN and the cause has been satisfactorily proved

The principal features of the behaviour over the globe of the solar semi-diurnal variation, as calculated by SIMPSON and others, are outlined The 'resonance theory', originally put forward by KELVIN, has been treated successively by a number of brilliant mathematicians with the idea that it must somehow be the answer LAMB showed how accurate the adjustment in period needed to be to give the magnification required Unfortunately the increasing body of knowledge about the many ways in which the atmosphere can arrange its flow from day to day and the great seasonal differences in the distribution of temperature in the upper air over the globe makes it hard for the meteorologist to accept any idea of fine and continuous adjustment Difficulties about other kinds of phenomena, such as the diurnal variations of turbulence and atmospheric electric potential gradient, which seem to be in some way interconnected with those of pressure, are not dealt with in this book and would, indeed, need a volume to themselves It is true that some of WHIPPLE's objections to the resonance theory are mentioned but they are brushed aside in a few lines That, however, need not detract from the value of the book as an account of the mathematical theory

A H R GOLDIE

Books to Come

Structure of Molecules Y K SIRKIN and M E DYATKINA, *Translated by* M A PARTRIDGE and D O JORDAN (*c 550 pp, illus, royal 8vo*) London Butterworths Scientific Publications Ltd

Metallkeramik, *Fourth edition* F SKAUPY (*c 280 pp; illus*) Weinheim/Bergstrasse Verlag Chemie GmbH *c DM 19 00*

Elementary Pile Theory H SOODAK and E C CAMPBELL · (*c 76 pp, 23 illus*) New York · John Wiley and Sons, Inc *c $2 50*

Preparation of Levulinic Acid

Use of Sodium Levulinate

L F WIGGINS, D Sc , Ph D , F R I C

The literature on the preparation of levulinic acid is reviewed The mechanism of the formation of this substance from carbohydrates is discussed and observations on the preparation of levulinic acid from sucrose recorded It is shown that levulinic acid is best prepared from sucrose when very dilute solutions are heated with hydrobromic acid Yields almost as high are obtained, however, when sucrose is heated with hydrochloric acid containing a small amount of bromide ion It is shown that crude cane juice can be used just as efficiently as pure sucrose in the preparation of levulinic acid A method whereby both levulinic acid and hydroxymethyl furfural are obtained from the same sample of sucrose is described The use of sodium levulinate as an anti-freeze agent is discussed

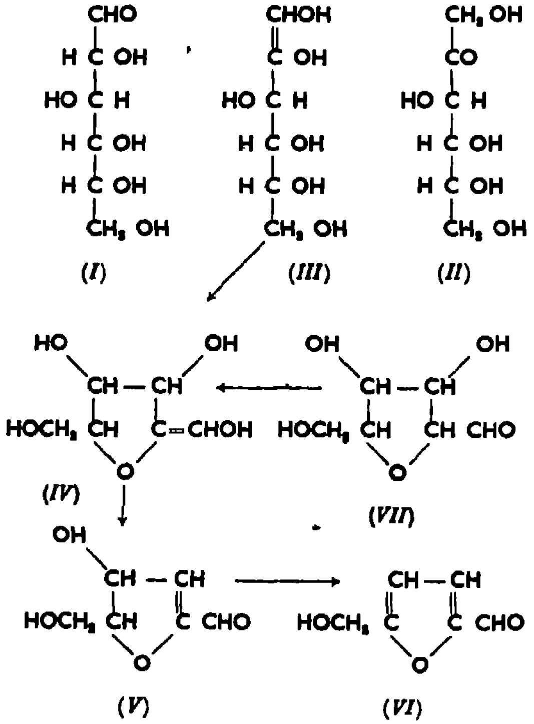
BECAUSE CH_3 CO CH_2 CH_2 COOH, levulinic acid, can be obtained from sucrose with reasonable ease its preparation and chemical properties are intimately bound up with the problem of the greater chemical utilization of sucrose A superficial examination of the molecular structure and properties of levulinic acid shows clearly that it is capable of a wide diversity of chemical reactions, producing many products of potential commercial value It has already been shown to give rise to a wide variety of organic compounds, but it is for the future to decide whether these compounds can be turned into products as industrially important as for example those from benzene or from the products of the petroleum industry The preparation of levulinic acid is therefore of prime interest and it is the object of this paper to discuss the problem of obtaining it from carbohydrates, and particularly from sucrose

Levulinic acid is an acid degradation product of all hexoses, of sucrose and other disaccharides, of polysaccharides containing hexoses, of glucosamine and 2-deoxypentoses Although sugars are the main sources of levulinic acid it can also be obtained from non-carbohydrates Both furfuryl alcohol[1] and 5-hydroxymethyl furfural[2] give levulinic acid on being treated with very dilute mineral acids It is also well known that levulinic acid can be obtained from rubber, through ozonolysis and subsequent oxidation[3] Simple terpenes, for example geraniol[4] and the carotenoids lycopene[5] and bixin[6], can be oxidized to give levulinic acid In addition the acid can be prepared by purely synthetic methods BRAUN and STOEHLE[7] obtained it by oxidation of allyl acetone and TIEMANN and SEMMLER[4] by oxidation of 2-methylhept-2-en-6-one Ethyl levulinate is formed when diethyl acetosuccinate is warmed with dilute hydrochloric acid[8] and levulinic acid when the acetylsuccinate is hydrolysed with alkali[9] It is also formed when ethyl diacetyl propionate is treated with alcoholic sodium methoxide[10]

The formation of levulinic acid from carbohydrates has long been known As early as 1840 MULDER[11] obtained levulinic acid by the action of mineral acids on sugars Many workers during the late nineteenth century studied its formation from all types of carbohydrates and showed that aldose sugars for example glucose[12], mannose[13], galactose[13, 14] and ketose sugars, for example fructose[15] and sorbose[16], gave levulinic acid on heating with mineral acids The ketoses gave rise to levulinic acid at a faster rate than the aldoses Amongst the disaccharides which were found to afford levulinic acid were lactose[16,17] sucrose[18] and the trisaccharide raffinose[19] Polysaccharides made up of aldose sugars also gave rise to levulinic acid on treatment with acid Thus inulin (polyfructose)[15, 20] and starch (polyglucose)[21] both gave levulinic acid upon suitable treatment BENTE[22] was probably the first to obtain it from cellulose The treatment of pentoses with mineral acids did not give levulinic acid , deoxypentoses, on the other hand, readily yielded it[23] HAMBURGER[24] found that glucosamine and the polysaccharide chitin gave levulinic acid on treatment with mineral acid The same author discovered that chitose, the product of the deamination of glucosamine, also furnished levulinic acid on comparatively mild treatment

MECHANISM OF FORMATION OF LEVULINIC ACID FROM CARBOHYDRATES

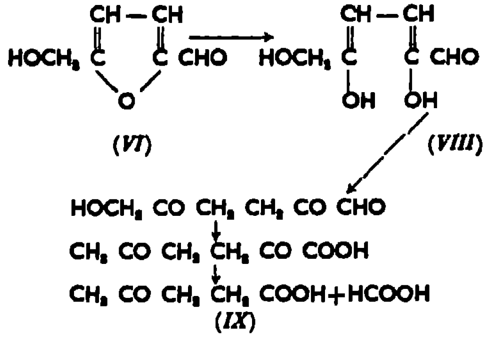
When sucrose is treated with acid the first result is the formation of fructose and glucose If these are written down in the open chain form as *I* and *II* it is readily seen that both give rise to one and the same 1,2-ene-diol, *III* and it is probable that this transitory ene-diol is all important in the conversion of hexoses to levulinic acid The next important step to consider is the formation of 5-hydroxymethyl furfural, *VI* from the transitory ene-diol *III* possibly through the stages *III*→*VI*



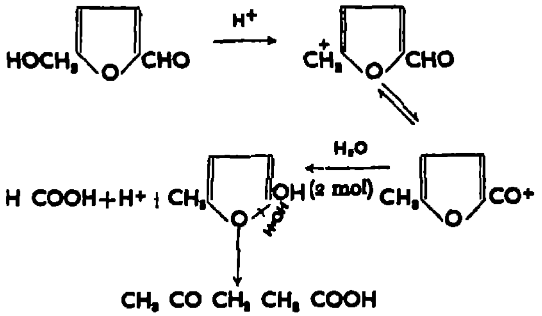
There is some factual basis for this scheme because chitose, the anhydro sugar obtained on deamination of glucosamine, which has the structure *VII*, can readily be converted into 5-hydroxymethyl furfural on being treated with 0·3 per cent oxalic acid[25] That hydroxymethyl furfural may easily be converted into levulinic acid and formic acid was clearly demonstrated by Teunissen[3] It appears therefore that the essential steps in the formation of levulinic acid from aldoses and ketoses are as follows

aldose or ketose → 1,2 ene diol → 5-hydroxymethyl furfural → levulinic acid + formic acid

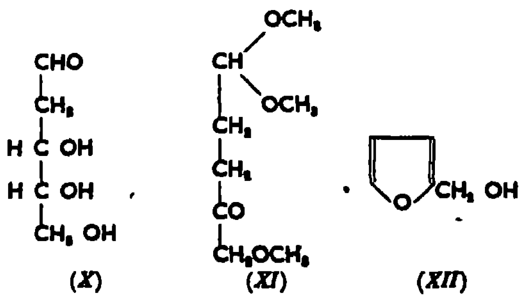
One possible course for the last step is represented by the changes *VI*→*VIII*→*IX*



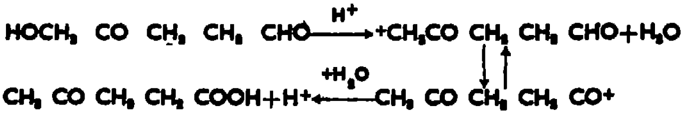
Burton[26] suggests the following scheme for the decomposition of hydroxymethyl furfural in the presence of H^+ into levulinic acid and formic acid and this probably represents as accurate an estimate of the course of the reaction as is possible with the knowledge at present available



It is of interest to speculate how levulinic acid may arise from 2-deoxypentoses It is known that 2-deoxyribose, *X*, on very mild treatment with methyl alcoholic hydrogen chloride gives ω-methoxymethyl levulinaldehyde dimethyl acetal[27], *XI* Also furfuryl alcohol, *XII*, on being treated with 0·1 per cent hydrogen chloride in methyl alcohol[28] gives rise to the same substance *XI* and that this on more drastic treatment gives levulinic acid



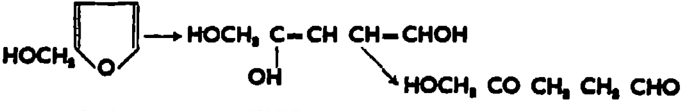
This latter transformation probably takes place after demethylation by a mechanism analogous to that suggested by Burton for the formation of levulinic acid from hydroxymethyl furfural.



$$HOCH_2\ CO\ CH_2\ CH_2\ CHO \xrightarrow{H^+} {}^+CH_2CO\ CH_2\ CH_2\ CHO + H_2O$$

$$CH_3\ CO\ CH_2\ CH_2\ COOH + H^+ \xleftarrow{+H_2O} CH_3\ CO\ CH_2\ CH_2\ CO^+$$

A possible intermediate in the conversion of furfuryl alcohol *XII* into hydroxymethyl levulinaldehyde *XIV* is the substance *XIII*, it is of significance that the 1,2-ene-diol of 2-deoxyribose, *X*, could theoretically be transformed into *XIII* Thus a common mechanism is provided for the formation of levulinic acid from such widely different substances as 2-deoxyribose and furfuryl alcohol



(*XII*) (*XIII*) (*XIV*)

Moreover it is also clear from this discussion that the same type of mechanism appears to operate in the conversion of all these different carbohydrate and furan derivatives into levulinic acid

EXPERIMENTS ON THE PREPARATION OF LEVULINIC ACID

Early workers, already mentioned, were not concerned with the preparation of levulinic acid in high yield, but this has been attained by modern methods

The preparation of levulinic acid as described in *Organic Syntheses*[29] involves heating sucrose (500 gm) or starch with water (1 l) and conc HCl (250 cc) for 24 hr at 100°C This treatment gives extensive amounts of humin material and only 21–22% yield of levulinic acid, which is obtained by ether extraction of the reaction mixture Later experiments carried out by the author and others and described herein have shown that this yield can be almost quadrupled

Most valuable work on the preparation of levulinic acid was that carried out by THOMAS and SCHUETTE[30], who discovered that levulinic acid was produced in much the same yield from glucose, fructose, sucrose or starch

In experiments designed to show the effect of acid concentration on the yield of levulinic acid, sucrose (250 gm) was heated with 600 cc of HCl of various concentrations and they obtained levulinic acid in yields from 34–42% of the theoretical as shown in *Table I*

Table I Effect of Acid Concentration on Yield

Per cent concentration HCl *in reaction solution*	*Temp °C*	*Pressure developed atm*	*Per cent yield levulinic acid*
2 3	162	7 0	34 8
4 6	162	7 0	42 4
7 5	162	7 0	41 3
3 2	145	4 5	36 2
4 8	145	4 5	35 4
7 8	145	4 3	37 1

Although Thomas and Schuette carried out all their experiments under pressure they state that increased pressure is advantageous Their results (*Table II*) show that increase of pressure from 2 0 to 7 0 atmospheres raises the yield of levulinic acid from 10 2 to 42 7 per cent The increased pressure however is obtained by using higher temperatures and their work does not eliminate the possibility that the increased yield is also due to the increased temperature It would seem certain that both variants play a part OST and BRODTKORB[31] clearly demonstrated that with glucose and 2 per cent sulphuric acid at lower temperatures the destruction of the sugar was far from complete Thus at 120°C for 8 hr, only 27 per cent of glucose was degraded and at 145°C for 7 hr, 75 per cent was destroyed

Table II Effect of Pressure on Yield

Temp °C	*Pressure atm*	*Time hr*	*Per cent yield levulinic acid*
120	2 0	1	10 2
130	3 6	1	31 5
145	4 5	1	34 3
162	7 0	1	42 7

They also showed that a heating period of at least 5 hr was needed to effect appreciable degradation of glucose under their conditions, see *Table III*

Table III Effect of Heating Period on Yield

Time hr	*Per cent destruction of glucose based on [α]D of solution*	*Per cent yield of levulinic acid, theoretical*	*Per cent yield based on glucose destroyed*
1 5	33	15 9	48
3 0	37 5	17 0	55
5 0	65	39 3	60
7 0	75	36 4	48

HAWORTH and WIGGINS[32] have made further studies on the preparation of levulinic acid from sucrose To discover the most effective mineral acid in converting sucrose into levulinic acid the former was heated with sulphuric, hydrochloric and hydrobromic acids under similar conditions, see *Table IV* The sugar was heated with the acid in sealed tubes at 140°C for 16 hr Additional data by BERTHELOT and ANDRE[33] showed that glucose and phosphoric acid at 160°C for 7 days gave only 37 per cent of levulinic acid

Table IV Effect of Catalyst Acid on Yield

Acid	*Per cent concentration acid*	*Per cent concentration sucrose gm/100 cc water*	*Per cent yield levulinic acid undistilled*
Sulphuric	9 1	6	42·3
Hydrochloric	9·7	6	60·0
Hydrobromic	9·0	6	70 0

It is clear from *Table IV* that hydrobromic acid is the best catalyst for the production of levulinic acid from sucrose The next most important fact discovered was that the yield of levulinic acid depended critically on the concentration of sucrose Using 50 per cent concentration of sucrose with 8 per cent hydrobromic acid, only 34 per cent of levulinic acid was obtained, but with 3 per cent sucrose under the same conditions the yield rose to 79 per cent Yields are based on weight of undistilled material These results are shown in *Table V* and *Figure 1* the solutions were heated at 140°C for 25 hr

Table V
Effect of Concentration of Sucrose on Yield

Per cent concentration hydrobromic acid	*Per cent concentration sucrose gm/100cc water*	*Per cent yield levulinic acid undistilled*
7 8	3 2	79
7 8	6 3	70
7 5	13 0	57
7 5	25 0	50
8 0	50 0	34

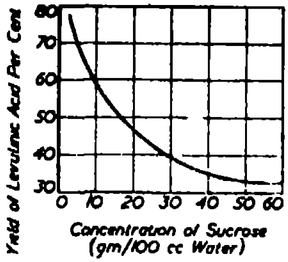


Figure 1 Variation in yield of levulinic acid with concentration of sucrose under the same experimental conditions

Since levulinic acid was most advantageously prepared using hydrobromic acid as the catalyst it was decided to test whether small amounts of bromide ion would be effective in increasing the yield of levulinic acid compared with that obtained using hydrochloric acid The results given in *Table VI* show that the addition of only 1 per cent sodium bromide to a hydrochloric acid solution of sucrose effected a marked increase in the yield under the conditions used This increase in the rate of a carbohydrate degradation reaction by bromide ion has been observed before in the case of the conversion of saccharic acid into furan 2, 5-dicarboxylic acid

Table VI Effect of Sodium Bromide on Yield

Per cent concentration hydrochloric acid	*Per cent concentration sucrose gm/100 cc water*	*Added substance*	*Temp of reaction °C*	*Time hr*	*Per cent yield°C levulinic acid, undistilled*
16 0	6 3	1 *per cent* NaBr	140	24	66 5
16 0	6 3	—	140	24	58 8
9 0	6 3	1 *per cent* NaBr	130	48	65 0
9 0	6·3	—	130	48	60 0
8·5	3·6	1 *per cent* NaBr	130	48	72 0
8 5	3·6	—	130	48	60 0

HAWORTH, JONES and WIGGINS[84] found that furan 2, 5-dicarboxylic acid could only be obtained from potassium saccharate and hydrochloric acid by heating the mixture at a high temperature *i e* at 140°C, under pressure, but when hydrobromic acid was used the reaction took place under atmospheric pressure and moreover gave a higher yield

The process of isolation of levulinic acid may be described as follows

After the dilute solution of sucrose had been heated with the acid reagents it was filtered from the black humin material, which was about 8% of the weight of sucrose used, and the clear solution was continuously extracted with ether in a conventional extraction apparatus The extract after being dried ($MgSO_4$) was evaporated at 40–50°C to a syrup this was heated to 100°C under reduced pressure, when formic acid (60–70% theoretical) distilled The residue crystallised completely on cooling and was weighed as levulinic acid It may be purified by distillation under good vacuum with but small (about 5%) loss The acid solution, after the removal of the levulinic acid by ether extraction, was boiled to remove dissolved ether, then heated with fresh sucrose and the process repeated After the first treatment slightly higher yields of levulinic acid were obtained The same acid solution could be repeatedly used without disadvantage Thus formic acid could also be conveniently isolated

PLOETZ[85] has also described methods of preparation of levulinic acid from carbohydrates using hydrobromic acid as the catalyst

Ploetz obtained 69% of levulinic acid from crude cane sugar, 75 3% from glucose and 64 4% from starch, by heating these carbohydrates with 10% hydrobromic acid at 130°C for 24 hr

THOMPSON[86] reports that if sodium chloride is added to a glucose/acid solution and the mixture heated at atmospheric pressure there is an increase in yield of levulinic acid The reason for adding the salt is, however, different from that obtaining in the addition of sodium bromide to the reaction mixture, and is doubtless merely to raise the boiling point of the solution

Other workers have prepared levulinic acid in the form of its methyl ester by heating sucrose (100 gm) for 10 hr at 160–165°C with methanol (320 gm) containing 2 5% hydrogen chloride and sodium sulphate, whence 1 4% of methoxymethyl furfural and 20 8% of methyl levulinate were obtained[87]

The following procedure for the preparation and isolation of levulinic acid is that used by the Staley Manufacturing Co of Chicago[88]

This involves the pre-heating of starch with dilute HCl (1 5–2 5%) at 100°C, then heating the mixture in a pressure digester at 190–200°C with mechanical agitation The temperature is raised by live steam at a rate of 1C° to 4C°/min The desired temperature is reached in 50–60 min and degradation of the sugar proceeds so that enough heat is liberated to maintain this temperature for a further ½ hr Thereafter the mixture is filtered free from a granular humin material partly neutralised to pH 1 9 and evaporated to small bulk NaCl which separates is centrifuged off and the mother liquor is subjected to steam distillation under vacuum, when a relatively pure form of levulinic acid of light colour together with a residual tar is obtained.

Recently MOYER[39] has found that purification of levulinic acid with sodium chlorite and hydrogen peroxide gave a water white product. The residual tar from the distillation yielded a further amount of levulinic acid by subjecting it to steam treatment followed by distillation[40]

Of the two possible methods of isolation of levulinic acid the solvent extraction process would appear to be the most favourable since it enables repeated use to be made of the acid catalyst and enables the easy isolation of formic acid to be achieved The solvent most often used is diethyl ether although the ratio of concentration of levulinic acid in ether to concentration of levulinic acid in water is 0 225 at 25°C and is not very high[41] MACALLUM[42] suggests that *n*-butanol is a better solvent than ether but this extracts a considerable amount of the mineral acid as well as the levulinic acid , since its b pt is rather high (118°C) some butyl levulinate must be formed during the extraction process Another solvent which preferentially extracts levulinic acid and not formic acid or the coloured by-products is methylene chloride[43] This has a low boiling point and is advantageous since its use offers no fire danger

Another process of interest to the problem of the utilization of sucrose as a basic chemical has been suggested[48] This is a two-stage process for the preparation of 5-hydroxymethylfurfural and levulinic acid from sucrose

> The sucrose is heated with oxalic acid, phosphoric acid, maleic acid or even very dilute hydrochloric acid, in an autoclave at 150 to 160°C for 3 hr These reagents degrade only the fructose half of the sucrose molecule and that only to 5-hydroxymethyl furfural After the weak acid treatment humin material is filtered off and the hydroxymethyl furfural is removed from solution by continuous extraction with ethyl acetate Thereafter the aqueous residue is evaporated to remove dissolved solvent, the appropriate amounts of hydrochloric acid and sodium bromide added, and the mixture heated under the conditions already mentioned to convert the residual glucose into levulinic acid

Obviously levulinic acid can be obtained not only from pure sucrose, but also from any hexose containing solution, for example molasses or crude cane juice[31] It has now been found, see *Table VII*, that crude cane juice can be just as efficiently converted into levulinic acid as pure sucrose

Table VII Yield of Levulinic Acid from Cane Juice

Per cent concentration acid	*Per cent concentration sugars*	*Added substances*	*Temp of reaction*	*Time hr*	*Per cent yield crude levulinic acid*
10 *hydrobromic*	3 8	—	140	16	77
„	7	—	140	16	60
9 *hydrochloric*	3 8	1 *per cent* NaBr	140	16	71

Cane juice was evaporated to a syrup containing 70 per cent solid and 65 per cent by weight of sugars (60 per cent as sucrose) This was heated in sealed tubes with acid reagents in the appropriate quantities as given in *Table VII* The levulinic acid formed in the reaction was isolated by the same solvent extraction procedure as that recorded above for pure sucrose

Table VII shows that under the most favourable conditions almost as high a yield of levulinic acid can be obtained from this carbohydrate source as from pure sucrose

Table VIII Physical Constants of Levulinic Acid

Boiling pt °C	*Melting pt °C*	*Refractive index n_D^t*	*Reference*
102–106/1 mm	—	—	46
105–108/2 mm	31	n_D^{40}, 1 4342	31
135/4 mm	—	—	44
137–139/10 mm	—	—	30
143–147/14 mm	—	n_D^{18}, 1 4420	47
245–246/760 mm	—	—	47
—	33	—	45
—	—	n_D^{18}, 1 4449	38

SODIUM LEVULINATE AS AN ANTI-FREEZE AGENT

When levulinic acid solution is almost neutralized with dilute sodium hydroxide and the solution evaporated to dryness, a crystalline sodium salt of good colour is obtained in practically quantitative yield Recrystallized from alcohol, the salt forms needles, m pt 168–170°C Sodium levulinate so prepared has been examined[48] as an anti-freeze agent at the Chemical Research Laboratory of the Department of Scientific and Industrial Research Its efficiency is satisfactory within the limits set by a eutectic point in the region of 40 per cent w/v although, weight for weight, it is not so efficient as ethylene glycol Being a solid, however, it has the advantage over glycol of greater convenience of transport Alternatively, it could be used as a 'stretching agent' for ethylene glycol in which it is soluble to the extent of approximately equal parts by weight of solute and solvent The behaviour of aqueous solutions of sodium levulinate at temperatures up to boiling (simulating the running conditions of an automobile cooling system) is satisfactory in respect to freedom from frothing and stability of *p*H and freezing point

A property of importance in an anti-freeze agent for heat exchange systems is the extent to which it will loosen rust and scale present on the metal surfaces over which the liquid circulates In radiator systems for example this may cause serious trouble through the choking of narrow waterways in the system Tests have shown that sodium levulinate has a greater rust-loosening action than tap water, although it is unlikely that the effect will be sufficiently marked to cause serious trouble Observations in the course of laboratory and car tests have revealed no deleterious action on rubber

Laboratory corrosion tests, using metals or combinations of metals likely to be present in car systems, have given satisfactory results except for some thinning of solder at soldered joints Additions of 1 per cent w/v of sodium chromate or sodium phosphate appreciably reduced this attack Car tests with 28 per cent sodium levulinate (f pt − 8 8°C) have confirmed its very satisfactory behaviour towards mild steel, they have also confirmed the corrosive action on solder and the tendency to the loosening of pre-existing rust Similar results were obtained with a solution of 10 per cent ethylene glycol and 15 per cent sodium levulinate (f pt 8 8°C), with an additional observation in respect to an aluminium alloy, *RR 50*, bolted either to mild steel alone or to mild steel and copper In ethylene glycol solution or in tap water either of these metal combinations leads to the greatest attack on mild steel In the presence of sodium levulinate the position is reversed, the greatest attack in each case being thrown upon the aluminium alloy, the corrosion of the steel being correspondingly reduced

Thus sodium levulinate could be used satisfactorily as an anti-freeze agent in many circumstances In heat-exchange systems there is no undue corrosion of iron or steel, either alone or in contact with other metals There is increased corrosion of the exposed surfaces of solder but the attack appears not to penetrate into the joints themselves and is probably amenable to suppression by the addition of a corrosion inhibitor Further research is required before sodium levulinate can be recommended for all conditions likely to arise in an automobile cooling system

The author is grateful to Professor Sir Norman Haworth, F R S, for his helpful interest in this work, to the Colonial Products Research Council for its support, to the Chemical Research Laboratory, Teddington, under whose auspices the tests on sodium levulinate as an anti-freeze agent were carried out, and to the Chief Scientist, Ministry of Supply, for permission to publish this paper

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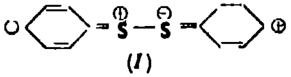
Research Correspondence

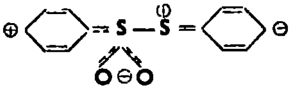
Ultraviolet Absorption Spectra of Some Aromatic Disulphides and Disulphoxides

RECENT publications by CARMACK *et alii* [1-3] and KOCH[4-6] prompt us to record here some observations made in these laboratories on a series of related aromatic disulphides and disulphoxides, the ultraviolet absorption spectra of which, determined in alcoholic solution, are summarized in *Tables I* and *II*. Absorption spectra of aromatic disulphoxides have not hitherto been recorded.

In the aromatic disulphides (*Table I*) both diphenyl[7] and di-*p*-tolyl disulphide[8] have λ_{max} approximately equal ($\Delta\lambda_{max}$ 60 Å) to that of thiophenol[4, 9-11] with ϵ_{max} double that of the mercaptan. This may imply direct electronic interaction between the two adjacent sulphur atoms, with numerous possible resonance forms such as *Formula I*, especially if it is assumed that the sulphur atom can function both as electron donor and acceptor, the latter assumption involving the concept of the expansion of its valency shell to ten electrons[12]. With di-*p*-cyanophenyl disulphide, λ_{max} has increased by 300 Å over the unsubstituted compound, an increment almost identical with that caused by the introduction of a cyano group [13, 14] into the isolated benzene nucleus. The imino-ether hydrochloride ($\Delta\lambda_{max}$ 320 Å) and amidine salts ($\Delta\lambda_{max}$ 410 Å) also show the behaviour expected by the introduction of one additional unsaturated linkage into the system, probably intensified in the latter by the additional internal resonance possibilities in the amidine system[15].



(*I*)



(*II*)

Table I. Aromatic Disulphides

Compound	λ max Å	log ε max
C_6H_5 S S C_6H_5	2,410	4 22
Me C_6H_4 S S C_6H_4 Me	2,420	4 29
NH_2 C_6H_4 S S C_6H_4 NH_2 2HCl	2,540–2 560 2 900	4 21 3 91
CN C_6H_4 S S C_6H_4 CN	2 670–2,730	4 41
EtO(NH)C C_6H_4 S S C_6H_4 C(NH)OEt 2HCl	2,710–2,750	4 31
NH_2(NH)C C_6H_4 S S C_6H_4 C(NH)NH_2 2HCl	2 800 2,840	4 38
NH_2(NH)C C_6H_4 S S C_6H_4 C(NH)NH_2 2C_6H_5 SO_3H	2,800–2,850	4 39

Table II. Aromatic Disulphoxides

Compound	λ max Å	log ε max
C_6H_5 S SO_2 C_6H_5	2 300 2 310 2,720*	4 15 3 60
CN C_6H_4 S SO_2 C_6H_4 CN	2,430 2 440 2,910*	4 40 3 85
NH_2CO C_6H_4 S SO_2 C_6H_4 $CONH_2$	2,400–2 440 2,830*	4 34 3 88
EtO(NH)C C_6H_4 S SO_2 C_6H_4 C(NH)OEt	2,490–2,500 2,830*	4 40 3 99
EtO(NH)C C_6H_4 S SO_2 C_6H_4 C(NH)OEt 2HCl	2,460–2,480 2,830*	4 39 3 96

*Inflection

In the corresponding disulphoxides (*Table II*) which are now generally accepted[16, 17] as possessing the unsymmetrical thiolsulphonate structure, one sulphur atom is devoid of unshared electrons. Structures such as *Formula II* may operate here, and the observed absorption maximum at 2,300 Å may be due to the reduced number of resonance possibilities as compared with both diphenyl disulphide and diphenyl sulphone. All disulphoxides examined show a characteristic inflection at 2,720–2,900 Å. Introduction of an additional unsaturated linkage into the *p*- and *p'*-positions, as in the diamide, dicyanide and di-iminoether, causes a shift in λ_{max} of only 120–170 Å showing the greatly reduced 'transmitting' ability of the thiolsulphonate as compared with the disulphide function.

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Frictional Properties of Porous Metal Impregnated with Plastic

IT has been shown earlier that any device which will produce a thin film of low shear strength on the surface of a harder substratum will, in general, give a low friction[1]. If the ploughing term is small the friction between the solids is approximately given by $F = As$, where A is the area of intimate contact and s shear strength at the interface. If both A and s are small, the frictional resistance will be low. Thus experiment has shown that if a thin film of indium (c. 10^{-4} cm thick) is deposited on to the surface of a hard metal, the friction at heavy loads may be as low as $\mu = 0.04$.

A film deposited on the surface may, by repeated sliding, be worn away, but this difficulty can be overcome by impregnating the harder material with the softer one. With a copper lead bearing metal, for example, the lead is dispersed throughout the copper, either as isolated droplets or as a continuous matrix in between the copper crystals. The sliding process itself then extrudes a thin film of lead over the surface of the copper and it is this process which is largely responsible for the low friction and wear[1].

Frictional measurement experiments on various plastics[2] have shown that solid *Teflon* [polytetrafluroethylene $(\text{–CF}_2\text{–CF}_2\text{–})_n$] gives a very low coefficient of friction when slid against metal surfaces.

Table I. Variation of Coefficient of Friction with Temperature

Types of copper	15°C	100°C	200°C	250°C	330°C	*After cooling to 20°C*
Impregnated with Teflon sintered	0.05	0.05	0.05	0.05	c. 0.12	0.05
Sintered un-treated	·4	·4	c. 0.7	c. 0.8	c. 1.2	c. 1
Solid	1.3	c. 1.3	c. 1	c. 1	c. 1	c. 1

It was found that a film of *Teflon* when simply rubbed on to metal surfaces would give a low value of the friction, but the film was worn away. Porous metal was, therefore, impregnated with the plastic. Sintered copper impregnated in this way (*Figure 1*) gave remarkably low values of friction. Some typical results are shown in *Table I*. Steel was used as the slider and the surfaces were unlubricated.

It will be seen that the treated metal gives a very low friction, $\mu = 0.05$, and this is maintained up to high temperatures. At 250°C. the friction is still

Figure 1. Section of sintered copper impregnated to a depth of c. 1 mm with Teflon. **a** *sintered copper.* **b** *impregnated surface layer (magnification × 10, reduced by 2/5 on reproduction)*

$\mu = 0\ 05$ At 330°C, where decomposition of the plastic would occur, the friction begins to rise to $\mu = 0\ 12$, but on allowing the metal to cool it decreases to $\mu = 0\ 05$ again The treated metal shows little sign of surface damage whereas the untreated copper displays marked adhesion, surface damage and wear

Since the thin plastic film can be fed on to the surface by the sliding process, it is not worn away by repeated sliding in fact repeated sliding leads to a reduction in the friction

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New Method for the Preparation of as-Dialkyl Hydrazines Bond Refractions and Bond Parachors of the N-N *and* N=N *links*

as-Dialkyl hydrazines $R_2N\ NH_2$ may be prepared by the reduction of the nitrosamines $R_2N\ NO$ with zinc and acetic acid, when R is methyl, ethyl or *n*-propyl The procedure is not suitable as a preparative method when R is *n*-butyl or a higher alkyl group , the dialkylamine is the main product We have found that the reduction of dialkyl nitrosamines by lithium aluminium hydride in dry ethereal solution provides a general method for the preparation of *as*-dialkyl hydrazines in excellent yields The hitherto unknown *as*-di-*n*-propyl, di-*n*-butyl and di-*n*-amyl hydrazines were readily obtained in good yields by this method , their physical properties are shown in *Table I*

Table I Physical Properties of some Dialkyl Hydrazines

Compound	*B p*	$d^{20°}_{4°}$	$n^{20°}_{D}$	R_D
$Pr^{\alpha}_2N\ NH_2$	31°/7 mm	0 7997	1 4266	37 29
$Bu^{\alpha}_2N\ NH_2$	61°/8 mm	0 8078	1 4319	46 54
$Am^{\alpha}_2N\ NH_2$	87°/7 mm	0 8107	1 4377	55 76

Utilizing the values for the bond refractions (D-line) and bond parachors previously reported[1] for C—H, C—C, C—N and N—H, the constants for the N—N link were computed from our measurements of the refractivities and parachors The results are given in *Table II*

Table II Bond Refraction and Bond Parachor for N—N *from as-Dialkyl Hydrazines*

Compound	*Bond refraction*	*Bond parachor*
$Et_2N\ NH_2$	2 04	7 9
$Pr^{\alpha}_2N\ NH_2$	2 03	6 7
$Bu^{\alpha}_2N\ NH_2$	1 98	5 8
$Am^{\alpha}_2N\ NH_2$	1 90	5 3
Mean	1 99	6 3

We have also calculated similar constants for this link from our experimental data on the di-*n*-alkyl nitrosamines The results are presented in *Table III*

Table III Constants for N—N *from Dialkyl Nitrosamines*

Compound	*Bond refraction*	*Bond parachor*
$Me_2N\ NO$	2 13	12 2
$Et_2N\ NO$	1 99	8 1
$Pr^{\alpha}_2N\ NO$	2 00	6 1
$Bu^{\alpha}_2N\ NO$	1 95	1 6
$Am^{\alpha}_2N\ NO$	1 87	−1 0
$(C_6H_{13}{}^{\alpha})_2N\ NO$	1 92	−3 1
Mean	1 98	—

It will be observed that the bond parachor decreases steadily as the molecular weight of the alkyl group increases

There are no satisfactory experimental data available for the calculation of the constants for the N=N link We have prepared and measured the refractivities and parachors of three azo-dicarboxylic esters ROOC N=N COOR The constants of the N=N bond were calculated with the aid of the data upon dialkyl oxalates[2] The results are collected in *Table IV*

Table IV Constants for N=N *from Azo-Dicarboxylic esters*

Compound	*Bond refraction*	*Bond parachor*
$EtO_2C—N=N—CO_2Et$	4 39	46 0
$Pr^{\alpha}O_2C—N=N—CO_2Pr^{\alpha}$	4 18	44 8
$Bu^{\alpha}O_2C—N=N—CO_2Bu^{\alpha}$	3 88	41 8
Mean	4 15	44 2

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Commentary: Scientific Research in Industry

SINCE 'KNOWLEDGE IS POWER', to quote an old saying, then experimental science must be the inspiration and guide of industry. Called into being by two needs irresistible to mankind, to live better and to know more, industry and science have naturally developed as it were in symbiosis. In Europe, the end of the eighteenth century marked the threshold of their great mutual renaissance. Now, a century and a half later, the factory has annexed the laboratory for direction, coordination and control, so that the physicist C. FABRY has drawn the bold but just simile of the internal secreting glands in a living body.

Meanwhile this union of science and industry has not come down through the ages unscathed. On the one hand there are those scientists in their ivory towers who gaze down on the earthy ground of practical application and decide it is far beneath them and hardly compatible with the dignity of their calling, and on the other hand there are industrialists who proclaim their disdain for scientific speculation. At the very heart of enterprise, we find the man in the workshop and the man in the laboratory at loggerheads: one styles his colleague 'empiricist' while the other retaliates with 'dreamer'.

Grieved at seeing science and industry behaving so much like the 'two ugly sisters', the famous scientist and engineer H. LE CHATELIER made himself champion of their union. He advised better understanding of the physicochemical laws underlying industrial processes, and at the same time mentioned the interest of men like A. L. LAVOISIER, J. A. C. CHAPTAL, C. L. BERTHOLLET and J. L. GAY-LUSSAC, in such things as lighting, bleaching and the manufacture of acids, which can hardly be said to have debased their scientific work.

Proud to have heard the call of this master and working under the encouragement of H. FAYOL, another pioneer of industrial research, the author devoted his career to the science of metallography in the special steels industry and he thanks the editor of *Research* for the chance of pleading a cause dear to him. Under the compulsion of brevity he will confine himself to the defence of two propositions:

1 that fundamental scientific research has its place alongside applied research in the laboratories of industry;

2 that industrial research should be spared the restrictions and sterilization which often result from too narrow a control.

Science in the works: importance of fundamental research—Two words serve to characterize the role of science in industrial enterprise: maintenance, improvement. To maintain the progress of works at the most satisfactory level is a delicate and laborious complex task; in industry as in war it is often easier to win than to hold. Modern industrial processes depend on so many factors that fluctuations of one or another are only to be expected. Such fluctuations are often the cause of long delays and costly rejections, and the only way of forestalling them is to subject all the governing factors to control This may be effected by frequent measurement or, better still, by a continuous recording of their magnitudes If, despite these precautions, the system of control breaks down, an expert examination is at once undertaken to determine the causes of deviation, so that a remedy may be found and recurrence of the trouble prevented

To improve is to perfect or recondition a process or plant, to raise the qualities of some existing product so as to increase its functional utility, or to create a new product to meet a new requirement This is the purpose of research it commences in the laboratory but continues in the workshop From initial conception to industrial application is usually a long and tortuous path, bristling with obstacles Research has two main branches first, scientific research, properly so-called and known as fundamental research , the other includes tentative applications, and is applied research

The boundary between these two is vaguely defined and the distinction occasionally a subtle one Both employ the same equipment and similar techniques, and results are obtained-by much the same methods The expected accuracy is not necessarily of a different order To find a difference, one must review the sources whence spring the motives for study and consider the morale of the scientist in the pursuit of his labours

Working at leisure and with no consideration of profit, the pure scientist can simply follow his bent in the choice of problems and methods of investigation He is even free to change his objective and pursue any side track which provokes his curiosity On the other hand the industrial investigator has a severe discipline and rigorous continuity of application imposed on him by industry His gamut of problems and their relative priorities are prescribed by the works, the consumers and the inventors , all are exacting and urgent.

The contribution of industrial laboratories to science is well illustrated by the whole history of metallography it is sufficient to recall the fundamental work of F Osmond, G Charpy, A. M. Portevin and others in France, and of such men as Sir William Roberts-Austen, R. A. Hadfield, A. Bain, and E Houdremont elsewhere Yet, in the present state of scientific organization in the great nations of the world, we find some good people who consider it desirable to limit the activities of industrial laboratories to applied research and to confine theoretical and fundamental research to central laboratories maintained by the state in establishments for higher learning or subsidized by professional bodies This seemingly logical thesis is too rigid and should be disputed On the strength of his forty years experience the author defends a more flexible arrangement, so as to make the best use of every worker's abilities, no matter where he may be employed With research, it is necessary to guard against too much planning for, say the Scriptures, ' The wind bloweth where it listeth ' Whoever carries out scientific research in industry cannot hope by his own efforts to discover every law and to assess every factor which comes into manufacture, but must be ready to assimilate other people's discoveries very quickly and take immediate advantage of them In addition to this receptive faculty he should have the advantage of some sort of intimacy with the subject of his research, for this confers an intuition in the solution of entirely new problems

The industrialist who accepts and encourages fundamental work alongside applied research enjoys a further, and perhaps more important, advantage in that he has recourse to the most efficacious means of insuring the scientific insemination of his undertaking

By this expression we are to understand that state of technical preparedness, by virtue of which all the executives of a given difficult task may know its true aim and understand the means of its achievement. The term must also embrace that state of cohesion which facilitates the swift and smooth running of the organization If the advantage of this scientific insemination is obvious in the harmonious flow of production, it is none the less certain on the social side

The benefits of this scientific insemination cannot be characterized better than by considering Fabry's physiological simile again. The pituitary gland excites other endocrine glands by means of the stimulants it secretes in the body and causes these glands to pour out into our blood the hormones which regulate the balanced growth and normal functioning of the organs Should, for example, the pituitary discontinue to provide the mysterious essence which stimulates the pancreas the latter will no longer secrete insulin and the body will suffer diabetes The pituitary regulates many other functions It is a control station not subservient to human will power and indeed quite distinct from the brain that is why it is called the endocrine brain Likewise in the industrial enterprise there is the thinking brain constituted by the directors, and complementary to this there is the endocrine brain consisting of the research services The one is as indispensable as the other

SCEPTICAL DISCOURSE ON THE PLANNING OF RESEARCH

The good seed sown by men like H le Chatelier has happily come to germination, and in France the advent of the harvest is full of promise Professional technical centres have been instituted, corporate laboratories built, and new Chairs and even new Schools have been founded to delve deeper into the science of metallurgy and diffuse its teaching All these measures prove that France, poorly endowed with raw materials with the exception of iron and aluminium, impoverished by the war but still rich in grey matter, sees the future of her industry in the conquest of quality

This industry should keep a sharp look out for the rocks, and for trouble even more formidable perhaps than past indifference to science In our anxiety to catch up after the war, and in our readiness to break old bonds, we have yet to fear lest controls impose a leaden shroud over science and research

Certainly, planning and everything under the heading of rational organization can work wonders when it comes to applied research or, more precisely, specific tasks The problem then is to draw industrial inferences, in the least time and at lowest cost, from some idea previously shown to be fertile, such inferences being already apparent and even amenable to calculation.

But it is another matter altogether for scientific research of a fundamental nature, which is indispensable for replenishing the reservoir with new ideas to form the basis for future technical progress To sail into the unknown, to follow a thread of Ariadne and explore a new domain, to draw back the curtain which veils the horizon of the investigator , these are achieved by intuition rather than by logic Such work is personal rather than collective, particularly in an individualistic country like France

Of course there have been rash minds who have laid claim to discerning in advance between purely speculative researches and those fertile in application Thus F. M Louvois, after the death of J B Colbert, begged the gentlemen of the Académie des Sciences to put an end to all 'useless and inquisitive' research so that they might devote themselves wholly to the development of arms and defence of fortifications This presumptuous minister of Louis XIV was truly unable to foresee the practical fertility of a multitude of disinterested studies Warned by the history of discoveries of resounding fame, our would-be realists should be more circumspect , for to predict whether any given study will bear fruit in industrial application, or just in a simple satisfaction of the intellect, is usually to go far beyond the bounds of human foresight

In his book *Science and the Planned State* J R Baker tells the strange story of an important therapeutic discovery the treatment of cancer of the prostate by means of folliculin He describes the tortuous meanderings of thought, the numerous blind alleys and unforeseen setbacks and then asks in conclusion

> What central planner, interested in the cure of cancer, would have supported Griffiths in his studies of the seasonal cycle of the hedgehog, or Grosser and Husler in their biochemical work on the lining membrane of the intestine ? How could anyone have connected phosphatase with cancer when the existence of phosphatase was unknown ? And while it was yet unknown, how could the man in charge of the cancer funds know to whom to give the money for research ?

These are words of wisdom, and the author, firm supporter of the same thesis, asks permission to set out for discussion his own story of an industrial discovery, of an alloy resistant in steam to corrosion fissuring.

STORY OF AN ALLOY

In 1912 a rust-proof chromium ferronickel with 24 per cent nickel and 2 per cent chromium was much used for steam turbine blades but had given disastrous results. After a few days running the blades would break and throw the turbines out of action. These fractures started as deep fissures several millimetres apart, originating near the surface and spreading between the crystals of the metal. The chemical origin was evident, and the activity of this corrosion cracking was in strange contrast with the general resistance of the alloy to superficial corrosion. Both metallurgists and designers shook their heads over this serious fault and introduced the phrase ‘the fallibility of ferro nickels’.

As he was then already devoted to the study of the thermal physics of these remarkable alloys, and being audacious as one is at twenty three, the author resolved to reinstate them, although without the faintest idea how he was going to achieve this rash undertaking!

The first thing to do was to reproduce the corrosion fissures *in vitro* and analyse their mechanism. Various bars, wires, foils, and plates of the sensitive alloy were enclosed in an autoclave coupled to a boiler and periodically taken out for examination. It was then found that the heaviest worked specimens were those most rapidly fissured, particularly those in which local hardening had set up considerable internal stresses. Since the annealed 24/2 nickel chromium alloy changed from a paramagnetic to a weakly ferromagnetic one on working, owing to a partial change of γ iron into α iron, the hypothesis came to mind that an alloy which was resistant to this phase change would also resist fissuring. So research was undertaken into iron-nickel alloys in which the $\gamma \rightarrow \alpha$ transformation did not take place. Dilatometric experiments were immediately carried out over the range −269 to 900°C, using Kamerlingh Onnes helium baths at the lower end of the scale, and it was shown that the only alloys meeting the requirement had the limiting composition Fe_2Ni with 34.45 per cent nickel. It now remained to be verified that this same nickel content coincided with the boundary of corrosion fissuring susceptibility.

At first, experiments seemed to justify this prophecy; specimens of invar, a ferronickel containing 36 per cent nickel, were withdrawn intact from the autoclave after six months treatment. Then one fine day several fissures were observed! Should the hypothesis be rejected in its entirety? Surely it held some element of truth, since the invar was only affected at some particular points; but there was something else as well.

During the next few months nothing turned up to elucidate this ‘other factor’. But, in 1914, CH-ED GUILLAUME, who was working in an entirely different field, made an important discovery. He had been studying, by means of the comparator at the Bureau International des Poids et Mesures, the slow slight spontaneous elongation of invar bars in the rolled condition (a few microns per metre per year), when it suddenly occurred to him that the traces of carbon in the alloy were the cause of its instability. On heating, the carbon dissolves in the ferronickel, remains in supersaturated solution after rapid cooling, and then slowly precipitates at ambient temperatures combined with iron and manganese as ternary cementite. To get over this, thought Guillaume, it should be possible to neutralize the carbon by addition of an element which would readily combine with it. Chromium was tried at once and found to be an effective remedy for this instability.

Some analogous phenomenon, or even the same one, might well account for the fissures. All the known facts were re-examined in the light of this second hypothesis, and appeared to favour the comparison. As soon as this was evident, the author made up his mind to try the same antidote. As prudence counselled the superposition of precautions prescribed by both hypotheses, he raised the nickel content from 24 to 35 per cent and the chromium from 2 to 11 per cent. This was on the right side of the Fe_2Ni boundary and the chromium should surely cope with the 0.3 per cent carbon which was essential for mechanical strength.

In the autoclave the new alloy proved wholly insensible to corrosion fissuring, and so it came to be used in steam turbines. Under the name of *ATV* it became an unparalleled industrial success from the year 1920 onward.

Nevertheless, was it safe to draw conclusions from a negative result? What guarantee was there that the dreaded fissures would not one day reappear? There was no scientifically established theory to rely on and the reputation of *ATV* rested solely upon empirical and therefore shaky knowledge. Furthermore, no one dared to alter the composition of the alloy in order to improve its mechanical properties. For this theoretical basis, so much needed and so actively sought after, we had to wait until 1928!

Thermomagnetic measurements on superhardened and tempered *ATV* had generally shown a magnetic transformation occurring over a range of temperatures, indicating the heterogeneous constitution of the iron-nickel-chromium-carbon austenite which formed an aggregate in the alloy with a complex cementite rich in chromium. The determination of these abnormal magnetization/temperature curves had fixed the amplitude and extent of this heterogeneity, of which the origin was evident: the centripetal migration of chromium towards each point where a complex cementite grain had been precipitated on annealing. At the same time, chemical tests had shown the existence of a sulphur reagent which was only slightly active towards high chromium ferronickels but which would attack strongly the chromium exhausted zones surrounding each of these grains. This all led without doubt to the conclusion that secondary heterogeneity on precipitation was the predominant factor in producing corrosion fissures.

From that time the reliability of *ATV* for use in steam turbines was established. However carefully the heat treatment of chromium ferronickel may be carried out, it is impossible to avoid the formation of chromium starved zones in some parts. The composition of an alloy must therefore be such that it will resist attack by its environment, not only in the mass but also at its more vulnerable regions. Hence the security conferred on *ATV* by its high nickel content, and the secret of its resistance to steam and water impurities regardless of its physicochemical and structural state and its micro-variations.

Not only has the theory provided an accredited confidence in *ATV*, but also, possibly more important, a basis for modifying its composition in order to raise its elastic limit and creep resistance without introducing doubts about its resistance to fissuring. Such elements as aluminium and titanium in effect form constituents with the nickel of the alloy which are more soluble at higher temperatures and are then able to participate in structural hardening on tempering and annealing, without a local reduction of the chromium content of the austenite as a result of their precipitation. The success of the heat resistant complex ferronickels due to this formula has been proved in practice, in the construction of gas turbines and jet propulsion units for aircraft.

Such, in brief, is the story of an alloy made in the factories of Imphy in France and in Hadfield's Hecla works in England, an alloy which has opened up the way for development of turbines on land and sea with a gross output of over ten million horsepower and which, according to Lord Dudley Gordon, has been a definite factor in the allied victory.

Suppose H. Fayol, having once posed the problem of alloys for the steam turbine, had taken upon himself to direct the research instead of delegating the task to the staff of his laboratory. He would probably have prescribed autoclave experiments, but whatever his genius he would certainly never have had the idea of including in his programme dilatometric experiments between 4 and 1,100°K, a range much greater than occurs in turbine practice. Still less would he have dreamed of asking Guillaume to investigate the instability of invar, a phenomenon of no apparent interest save to the specialist in metrology. These delicate studies, having no seeming connection with corrosion fissures, threw light on the results of the autoclave experiments and made them fruitful.

In conclusion the author hopes that many young workers will come into the laboratories of industry, and that there they will find the great satisfaction that he has gleaned. He hopes that their masters, like Fayol, will help, guide and encourage their enthusiasm, and will permit the full flowering of their individual personalities. He expresses the wish that their efforts will always achieve peaceful ends, in mitigating the burdens of mankind and in raising the standard of living.

P. Chevenard

Applications of the Electronic Theory of Organic Reactions

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UNTIL recently organic chemistry was more of an art than an exact science, its practitioners relying mainly on intuition and empirical generalizations of doubtful validity Only in the last thirty years has the study of organic reactions been placed on a logical basis, by the development and application of modern atomic theory and physicochemical methods

Ideally chemistry has now been reduced by the physicists to problems in pure mathematics, by solving the relevant Schrödinger equations it should be possible to predict in detail the course of any reaction, however complicated At present, however, the solution of such equations is hopelessly impracticable and the best line open is the development of a qualitative theory, based on very approximate quantum mechanical calculations, which will enable reactions at least to be interpreted and correlated

A successful qualitative theory of this kind was first devised by A LAPWORTH and R ROBINSON[1], the so-called electronic theory of organic chemistry, in terms of the Bohr-Lewis model of the atom This theory proved extraordinarily successful and it has since been consolidated and extended by various physicochemical and quantum mechanical investigations[2] It is extremely unlikely that any proposed reaction mechanism can be correct if it is at variance with the conclusions of electronic theory in its present form

To be acceptable, therefore, a reaction mechanism must not only account for the products and kinetics of a reaction but it must also be electronically reasonable From this point of view much of the effort that is being spent today in the study of organic reactions is misspent, the results could have been predicted out of hand The object here is to indicate the kind of guidance that the electronic theory can provide and, incidentally, to illustrate some of its latest developments Examples have been chosen deliberately for their technical importance

DIAZONIUM SALTS AND THEIR REACTIONS

Formation— Diazonium salts are usually prepared from primary aromatic amines and nitrous acid in acid solution, according to the reaction

$$RNH_2 + HNO_2 + \overset{+}{H} \rightarrow R\overset{+}{N}\equiv N + 2H_2O \quad ..(1)$$

Since it is known that N-nitrosamiline is converted by acids into diazonium salts, and since secondary amines under conditions similar to reaction 1 form nitrosamines, it can reasonably be assumed that the initial step in diazotization is the formation of a primary nitrosamine Given this information, the mechanism can be deduced

Nitrous acid is electronically analogous to a carboxylic acid RCOOH; the formation of a nitrosamine from a nitrous acid derivative NOX should be analogous to the formation of an amide from the corresponding derivative RCOX This analogy suggests that the former reaction is also a bimolecular anionoid replacement

$$RN\overset{\curvearrowright}{H_2}\ \ \overset{\curvearrowright}{NO{-}X} \rightarrow RNH\ NO + \overset{+}{H} + \overset{-}{X} \quad . \quad (2)$$

$$RN\overset{\curvearrowright}{H_2}\ \ \overset{\curvearrowright}{RCO{-}X} \rightarrow RNH\ COR + \overset{+}{H} + \overset{-}{X} \quad . \quad (3)$$

Diazotization should therefore involve the free amine and not its salt, at all events the ion $R\overset{+}{N}H_3$, where N is covalently saturated, could hardly be involved. Reaction 2, like reaction 3, should occur more readily the more cationoid X i e the stronger the acid HX, N_2O_3 ($X = NO_2$) and NOCl or NOBr should react more readily than HNO_2 Also increase in anionoid activity (basicity) of RNH_2 will facilitate reaction, although this effect may be masked to some extent by the decrease in concentration of free amine present in the acid medium Amines of low basicity may be diazotized only by very strongly cationoid derivatives of nitrous acid And, finally, reaction 2 should occur more easily than reaction 3 since N has a greater electron affinity than RC.

These conclusions are all known to be correct. Kinetic studies[3] have shown that diazotisation involves the free amine and not its salt and that reaction takes place not with free nitrous acid, but with more cationoid derivatives (N_2O_3, NOCl) formed from it in acid media; diazotizations take place much faster than reactions of amines with analogous carboxylic acid derivatives; and amines of very low basicity *e.g.* picramide can be diazotised only by the solutions of nitrous acid in strong mineral acids which contain the cation NO^+ (the most cationoid derivative possible from nitrous acid).

Stability—The heat of formation of nitrogen is abnormally high ; therefore diazonium cations might be expected to lose nitrogen readily, reaction 4 being exothermic.

$$\mathrm{R{-}\underset{\circlearrowright}{\overset{+}{N}}{\equiv}N \rightarrow \overset{+}{R} + N_2} \qquad (4)$$

Aliphatic diazonium salts are in fact unstable, decomposing at once to give nitrogen and products derived from R$^+$. Aromatic diazonium salts are, however, mesomeric and are thus sufficiently stabilized to be isolatable , the cation $\mathrm{R{-}\overset{+}{N}{\equiv}N}$ is electronically analogous to R–C≡CH or R–C≡N

Clearly reaction 4 will be inhibited by increase in cationoid activity of R , since the same factor will make the amine RNH$_2$ less basic, the stability of a diazonium salt should be greater the less basic the amine from which it is derived. Aryldiazonium salts are usually dangerously unstable in the free state, but the stability rises with increasing cationoid activity The salts derived from weak bases *e g* sulphanilic acid are often quite safe to handle and are used in the production of azoic dyes (azo dyes formed by coupling inside the fibres of a fabric)

The Sandmeyer reaction—The decomposition 4 of diazonium salts is analogous to the first step in a monomolecular aliphatic replacement reaction , for example, the solvolysis of *tert*-butyl chloride in aqueous alcohol, where the chloride first ionizes to Bu$^+$ and Cl$^-$ Analogy suggests that reaction 4 should have a bimolecular counterpart, and that this reaction

$$\overset{-\curvearrowright}{\mathrm{Y}}\ \ \mathrm{R{-}\overset{\curvearrowright}{N}{}_2^{+} \rightarrow RY + N_2} \qquad (5)$$

should be facilitated by increase in cationoid activity of R That is, reaction 5 should occur more readily with the more stable diazonium salts derived from the less basic amines

The Sandmeyer reaction of strongly cationoid diazonium salts seems to follow this mechanism, Y$^-$ being a complex anion which breaks down during the reaction, *e g* CuCl$_2^-$ which acts as a potential source of Cl$^-$. The reactions are clean and give good yields and, as H H. HODGSON[4] has shown, several other halides (FeCl$_3$, CoCl$_2$) are as effective catalysts as cuprous salts The action of the catalyst is uncertain ; possibly the catalytic effect is due to the greater deformability of the complex anion which facilitates the approach of the diazonium cation Iodide, the most deformable halide ion, reacts without a catalyst. Quantitative data are lacking on the relative rates of reaction, but the reactions are certainly smoother with the more cationoid diazonium salts. Moreover many of these will react with hydrochloric acid in absence of a catalyst, and the hydrolysis of the more cationoid diazonium salts (equation 5 with Y$^-$ = H$_2$O) certainly takes place more easily Diazopicramide is hydrolysed at once by ice-cold water

The Sandmeyer reaction of less cationoid diazonium salts is more complicated , these reactions are tarry and are specifically catalysed by cuprous salts Here the ionic mechanism 5 should be less favourable and probably the reaction catalysed by Cu$^+$ involves a redox cycle with free radical intermediates, as W A WATERS[5] has suggested ·

$$\begin{gathered} \mathrm{RN_2^+ + CuCl_2^- \rightarrow R + N_2 + CuCl_2^-} \\ \mathrm{R + CuCl_2^- \rightarrow RCl + CuCl_2^-} \qquad (6) \end{gathered}$$

The specific effect of copper can be ascribed to its unique characteristic of having two valency states of comparable stability differing by one valency unit. This mechanism provides an attractive explanation of the Pschorr reaction , the intermediate aryl radical cyclizing Obviously mechanism 6 cannot apply in the reactions studied by H H Hodgson, where catalytic action is not specifically confined to cuprous salts

Coupling reactions—The diazonium cation RN$_2^+$ is electronically analogous to the nitrile RCN , each contains a triple bond between atoms of unlike electron affinity In the nitrile N has a greater electron affinity than C , in the diazonium cation 4-covalent N$^+$ has a higher electron affinity than 3-covalent N Now anionoid reagents can attack the C≡N bond of nitriles , for instance Grignard reagents or HO A similar attack on a diazonium cation should give an azo-compound

$$\mathrm{R{-}\underset{\circlearrowleft}{\overset{+}{N}}{\equiv}N}\ \ \overset{\curvearrowleft\ -}{\mathrm{Y}} \rightarrow \mathrm{R{-}N{=}N{-}Y} \qquad (7)$$

The most important example of mechanism 7 is the coupling reaction with phenols and aromatic amines to give azo dyes According to mechanism 7, these reactions should involve the free diazonium cation and Y$^-$ in its most anionoid form , that is, phenols should couple as phenate ions, and aromatic amines as free bases These conclusions have been confirmed by kinetic studies[6] The rate of reaction should increase with increasing cationoid activity of R and increasing anionoid activity of Y$^-$. In fact cationoid substituents (*e g* SO$_3$H, NO$_2$) in R increase, anionoid (alkyl, *o* · *p*-RO, R$_2$N) decrease the rate of coupling[7] , while phenols couple only as free phenate ions and not as ethers or less anionoid derivatives.

Equations 6 and 7 represent alternative modes of reaction. From a consideration of bond energies and since bonds between nitrogen and hetero elements are weak, it is evident that reaction 7 will be most favourable if it leads to the formation of a C–N bond.

Thus carbonium and cyanide ions also couple; many such products from acetoacetate derivatives are important pigments and dyes

Reduction— Diazonium salts should be reduced more readily than nitriles, since the group N_2^+ has a much greater electron affinity than CN Such reductions do take place quite easily The first product is probably an azo compound

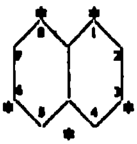
$$RN_2^+ + H^+ + 2e \rightarrow R{-}N{=}NH \qquad (8)$$

In acid solution, with a strong reducing agent, this is reduced in turn to a hydrazine, otherwise it decomposes to RH and N_2 Reduction by alcohols probably follows mechanism 8, the alcohol acting as a source of H^- $(\overset{\curvearrowright}{\mathrm{HO}}{-}\overset{|}{\underset{|}{\mathrm{C}}}{-}\overset{\curvearrowright}{\mathrm{H}})$ Alcohols are weak reducing agents, deamination with alcohol therefore gives good yields only with strongly cationoid diazonium salts With less cationoid diazonium salts, ethers are formed by decomposition (equation 4) and combination of the resulting aryl cations with the solvent Carbonium ions are known to attack the oxygen of alcohols rather than α-hydrogen

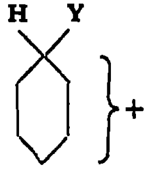
AROMATIC SUBSTITUTION

Aromatic compounds may be substituted by all three types of reagent cationoid, anionoid or radical, but the cationoid substitutions are the most important The interpretation of these reactions was the greatest triumph of the classical electronic theory, curiously enough it is just this part of the classical theory that now requires most modification. In the classical treatment, aromatic compounds were regarded as tautomeric mixtures of Kekulé-type isomers, and the possible electron displacements in such isomers were discussed Since aromatic compounds are now known to be mesomeric and not tautomeric, the treatment cannot be applied In its place, however, we can use a generalization deduced by C A COULSON and H C LONGUET-HIGGINS[8] from quantum mechanical reasoning This may be stated as follows 'In the formula for the aromatic structure, star alternate atoms so that no two starred and no two unstarred atoms are bonded This is always possible unless odd-numbered rings are present, as in azulene Then an anionoid (cationoid) substituent on a starred (unstarred) atom increases the anionoid (cationoid) activity of unstarred (starred) atoms, but to a first approximation leaves the starred (unstarred) atoms unaffected' This leads to the same rules for general orientation as the classical theory Thus anionoid substituents increase the *ortho* · *para* anionoid activity and are *ortho* *para* directing, while cationoid substituents decrease the *ortho* · *para* anionoid activity and are *meta*directing

The rule is especially useful in more complicated systems, to find out whether a given substituent will affect a given position For instance, it can be predicted at once that an α-substituent in naphthalene will affect the 5 7 positions, a β-substituent the 6 8 positions, see formula *I* In fact, α-nitronaphthalene substitutes mainly 6 8, β-nitronaphthalene mainly 5 7, the cationoid nitro group deactivating the other pair of positions in each instance



(*I*)



(*II*)

This qualitative treatment does not distinguish between the reactivities of equivalent positions (starred or unstarred), it cannot for example predict the relative amounts of *ortho* and *para* isomers in benzene substitution, nor the orientation in substitution of more complicated hydrocarbons These problems can be solved by a method due to G W WHELAND[9], which can be illustrated most clearly in benzene substitution Wheland pointed out that the transition state must approximate to the 'quinonoid' structure *II* Now the resonance energy of such an ion can be calculated, and should be a measure of the internal energy of the transition state for substitution Therefore if the effect of substituents on this energy is calculated, the relative stabilities of the possible transition states for reaction of a substituted benzene can be deduced, and so the relative yields of various isomers predicted Wheland showed that the usual rules for orientation in benzene could be derived in this way, and also the fact that naphthalene substitutes mainly α Recently the author has extended this treatment further and deduced the following rules for predicting *ortho* · *para* ratios in the substitution of a benzene derivative C_6H_5X

1. If X is an inductive substituent, or an anionoid electromeric substituent, the *ortho* *para* ratio falls with increasing electron affinity of X and is generally < 1 This is found to be so in the series X = CH_3, CH_2Cl, $CHCl_2$, CCl_3, and X = I, Br, Cl, F
2. If X is a cationoid electromeric substituent, the *ortho* *para* ratio rises with increasing electron affinity of X and is always > 1. This is seen in the series R = EtOOC, HOOC, NO_2

By applying these rules and assuming that the effect of substituents is additive, orientation in polysubstituted benzenes can be predicted

The Friedel-Crafts reaction—This reaction is a cationoid aromatic substitution by alkyl or acyl cations, the latter being formed from the corresponding halides by the action of aluminium halide

$$\overset{\curvearrowright}{\mathrm{R-X}}\ \mathrm{AlX_3} \rightarrow \mathrm{R^+\ AlX_4^-}$$
$$\mathrm{R^+ + ArH \rightarrow ArR + H^+}$$

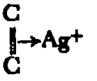
This mechanism has been established by two lines of evidence First, conductivity[10] and dipole measurements[11] show that the organic halide and aluminium halide combine to give a saline intermediate, and secondly, use of radioactive indicators establishes that during reaction complete exchange of halogen takes place, this can only be explained if the symmetrical anion $\mathrm{AlX_4^-}$ is formed as an intermediate The reaction usually follows the standard orientation rules for cationoid substitution and likewise is facilitated by anionoid substituents in the aromatic nucleus Cationoid substituents retard the reaction, as theory would predict, nitrobenzene fails to react Similar substitution reactions are given by alkyl cations prepared in other ways, from olefins and acids ($\mathrm{H_2SO_4}$, HF), $\mathrm{C{=}C + H^+ \rightarrow CH{-}C^+}$, or by S_1 ionization* of oxonium salts, formed from alcohols with strong acids or $\mathrm{BF_3}$

The most interesting reactions of this type are the alkylations of alkylbenzenes, since the orientation is normally *meta* and not *ortho-para* Thus methylation of toluene gives *m*-xylene as the main $\mathrm{C_8}$ hydrocarbon The explanation is that these reactions are reversible, therefore an equilibrium mixture of products is obtained, the composition of which is determined by the relative thermodynamic stabilities of the isomers, not by their rates of formation Independent measurements show that *m*-xylene is in fact the most stable dimethylbenzene Friedel-Crafts acylation reactions give 'normal' products, since the latter are ketones and are removed from the system by coordination with aluminium halide The reactions are not reversible Another important example of 'abnormal' orientation due to reversibility is the β-sulphonation of naphthalene at high temperatures, apparently the α-isomer is the less stable, but predominates at low temperatures when the sulphonation is effectively irreversible At high temperatures the reverse reaction (hydrolysis of the sulphonic acid) becomes appreciable and the more stable β-isomer is obtained.

MOLECULAR REARRANGEMENTS

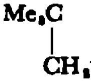
A molecular rearrangement[4] is a reaction in which a group migrates from one point in a given molecule to another. In a true rearrangement the process is intramolecular, the migrating group never being completely detached from the parent molecule Until recently the mechanism of these reactions remained obscure since it was difficult to see any way in which the migrating group could be held during migration, and the evidence often seemed conclusive that the groups were firmly held throughout The explanation of these reactions is interesting since it could not possibly have been anticipated on classical grounds

According to the quantum mechanical treatment, the C=C double bond in ethylene differs qualitatively from the C–C single bond in ethane The double bond is a combination of a normal single (σ) bond with a π-bond, in the latter the electron density is concentrated in streamers above and below the line joining the nuclei and not, as in a σ-bond, along that line, *Figure 1* Now the electron distribution in the π-orbital is very similar to that in an atomic *p*-orbital, for instance the distribution of one of the unshared electrons of oxygen, and apparently there is no theoretical reason why the π-electrons should not, like *p*-electrons, be used to form dative bonds The most direct evidence that such molecular bonds can be formed is the existence of coordination compounds of olefins in which the olefin acts as a single donor centre, for instance with silver salts the



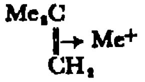
$\mathrm{C{=}C \rightarrow Ag^+}$

(*III*)



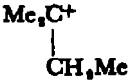
$\mathrm{Me_3C{-}CH_2^+}$

(*IV*)



$\mathrm{Me_2C{=}CH_2 \rightarrow Me^+}$

(*V*)



$\mathrm{Me_2C^+{-}CH_2Me}$

(*VI*)

complex cation *III* is formed In this π-complex, silver will be attached more or less symmetrically to the C=C bond, and not to either of the carbon atoms, hence the term molecular bond

Now the large group of carbonium ion rearrangements[12] can at once be explained in terms of π-complex intermediates Consider for instance the neopentyl cation *IV* This cation is isomeric with the π-complex *V*, the cation can isomerize to *V* by migration of methyl from carbon to the adjacent bond, and then by further migration the *tert*-amyl cation *VI* can be formed The π-complex provides the necessary intermediate for migration without detachment of the migrating group

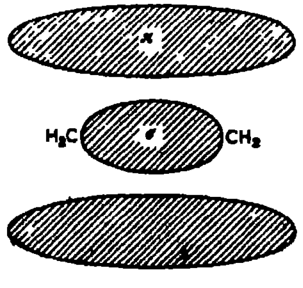


Figure 1 Distribution of electrons in the C=C *bond*

This idea can be applied more strikingly to aromatic systems. According to quantum theory, the atoms in an aromatic ring are linked by single (σ) bonds, and by π-bonds formed by completely delocalized π-electrons, the electrons in these π-bonds occupy orbitals, each of which covers the whole aromatic system For instance in benzene the π-orbitals form rings of electron density above and below the ring of nuclei, Figure 1 Now an acceptor atom or group should be able to attach itself to these rings of electron density and then be relatively free to move round them, the π-electrons providing a kind of electronic tramway by which groups can migrate round the ring, being firmly held all the time by coordinate bonds It is impossible in the space available here to discuss this theory more fully, it does enable one to explain in a most satisfactorily comprehensive way the whole range of known molecular rearrangements In particular it provides a simple interpretation of the most complex and technically important of them, the benzidine rearrangement, predicting correctly which of the various possible products will be formed in any given instance

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* S_1 represents unimolecular, S_2 bimolecular reactions

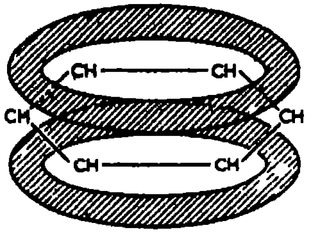


Figure 1 Distribution of π-electrons in benzene

ALUMINIUM CHLORIDE CATALYSIS IN PETROLEUM TECHNOLOGY

One of the technically most important fields in which the π-complex theory should prove useful is the chemistry of various catalysed reactions of hydrocarbons In the presence of aluminium chloride, sulphuric acid *etc* paraffin hydrocarbons can undergo the most extraordinary contortions It now seems fairly clear that alkyl cations are the reactive intermediates, and reasonable mechanisms have been devised for some of the simpler reactions, for instance the alkylation of *iso*butane by *iso*butene in presence of sulphuric acid.

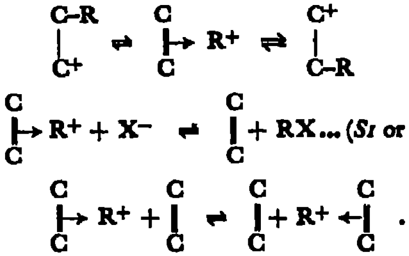
$$\mathrm{Me_2C{=}CH_2 + H^+ \rightarrow Me_3C^+}$$

$$\mathrm{Me_3C^+ + Me_2C{=}CH_2 \rightarrow Me_2\overset{+}{C}{-}CH_2{-}CMe_3}$$

$$\mathrm{Me_2\overset{+}{C}{-}CH_2{-}CMe_3 + Me_3\,CH}$$
$$\mathrm{\rightarrow Me_2\,CH\,CH_2\,CMe_3 + Me_3C^+} \qquad (9)$$

This mechanism, on electronic grounds, must be correct, but it is by no means generally accepted Unfortunately *iso*butene is the only olefin which reacts in so simple and clear cut a manner. The reactions[18] with 1- and 2-butenes give, it is true, octanes as the main products, and the predominant octane isomers formed can be interpreted in terms of reactions 9 above if a carbonium ion rearrangement of the intermediate octyl cation precedes its attack on *iso*butane However, together with these reasonable products a surprising mixture of hydrocarbons is obtained, containing isomeric pentanes, hexanes, heptanes, octanes and nonanes and unidentified higher hydrocarbons These can only be formed by dismutation and transalkylation reactions, analogous to those which occur in the aluminium chloride-catalysed cracking of hydrocarbons Most of the workers in the field are engaged in trying to find out what these reactions are and their mechanisms, but progress has been slow

It seems possible on purely electronic grounds to make certain predictions which will greatly facilitate this work, if it is assumed that the intermediates are carbonium ions The possible reactions of such ions in a system containing paraffins and olefins seem to be limited to the following.



$$\begin{array}{c}\mathrm{C{-}R}\\ |\\ \mathrm{C^+}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{C}\\ \| \!\rightarrow \mathrm{R^+}\\ \mathrm{C}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{C^+}\\ |\\ \mathrm{C{-}R}\end{array} \qquad (10)$$

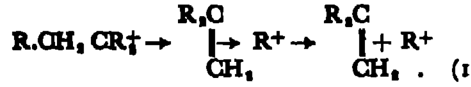
$$\begin{array}{c}\mathrm{C}\\ \| \!\rightarrow \mathrm{R^+}\\ \mathrm{C}\end{array} + \mathrm{X^-} \rightleftharpoons \begin{array}{c}\mathrm{C}\\ \|\\ \mathrm{C}\end{array} + \mathrm{RX} \ldots (S_1 \text{ or } S_2) \qquad (11)$$

$$\begin{array}{c}\mathrm{C}\\ \| \!\rightarrow \mathrm{R^+}\\ \mathrm{C}\end{array} + \begin{array}{c}\mathrm{C}\\ \|\\ \mathrm{C}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{C}\\ \|\\ \mathrm{C}\end{array} + \mathrm{R^+} \leftarrow \begin{array}{c}\mathrm{C}\\ \|\\ \mathrm{C}\end{array} . \qquad (12)$$

$$\mathrm{R^+ + R'H \rightleftharpoons RH + (R')^+} \qquad (13)$$

Reaction 10 is a normal carbonium ion rearrangement Reactions of this kind can enable any carbonium ion to come into equilibrium with all its isomers, naturally the most stable ions, trialkylcarbonium, will predominate Reaction 11 is a dismutation by which carbon chains can be broken at any point, it also provides a molecule of olefin which can be converted to a carbonium ion by the catalyst The reverse reaction provides a mechanism for polymerization Reaction 12 is a transalkylation, and reaction 13 enables unreactive paraffins to be brought into a reactive state. Therefore only a small amount of olefin is necessary to provide the initial carbonium ions, more can be formed during the reaction by mechanism 11, and the activity can always be transferred through the system by reaction 13. The reactions are really ionic chain reactions and a small amount of chain carrier (cation) will suffice Moreover the heats of reactions 10–13 are probably quite small and so too in all probability are their activation energies The extraordinary speed with which aluminium chloride isomerizes hydrocarbons at low temperatures can therefore easily be explained; and the reactions are theoretically sufficient to explain the conversion of any aliphatic hydrocarbon into any other.

For lack of data it is impossible to apply these principles in detail Three general points may be made. First, it is easy to explain the tendency for paraffins to crack into branched C_4 units A carbonium ion will isomerize rapidly to an ion R_3C^+, since tertiary ions are the most stable Fission by reaction 11 will then reduce one side chain to methyl, *e.g*



$$R.CH_2CR_2^+ \rightarrow \overset{R_2C}{\underset{CH_3}{|}} \rightarrow R^+ \rightarrow \overset{R_2C}{\underset{CH_2}{\|}} + R^+ \quad . \quad (14)$$

followed by reaction with the catalyst, a proton source *e g* $AlX_3 + HX$ Hydrogen halides are necessary as promoters in aluminium halide catalysis[14]

$$R_2C{=}CH_2 + \overset{+}{H} \rightarrow R_2\overset{+}{C}Me \quad . \quad (15)$$

The other side chains then split likewise Secondly, the reactions

$$C{=}C + HX \rightleftharpoons \overset{+}{C}{-}CH + X^- \qquad (16)$$

are likely to be rapid Since there is no reason why the hydrogen removed by X^- should be the same one that originally attacked the double bond, reaction 16 should lead to a rapid equilibration of hydrogen between hydrocarbons, and between them and the catalyst These conclusions have been confirmed by experiments with deuterium compounds[15] Thirdly, in interpreting actual reactions in terms of the scheme suggested here, it should be remembered that reactions 10, 12 and 13 will tend to convert less stable cations into more stable ones, and that fission of π-complexes by mechanism 11 will occur less readily the more anionoid the resulting olefin or the less anionoid R

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Fluidization of Masses of Particles

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WHEN an upward stream of gas or liquid is passed through a supported and laterally confined mass of solid particles reproducible changes in physical behaviour are observed which go through successive stages as the fluid velocity is increased The present discussion is focused particularly upon one stage in which the mass is continuously agitated by the rising fluid to form a bed of moving, interacting particles Such a bed is bounded by a free upper surface or zone of discontinuity that is subject to wave motion Under certain circumstances part of the rising fluid may pass through the bed in the form of pockets or bubbles. The suspended mass is mobile, it yields to an external force and may be caused to flow through pipes and valves by means of gravity head A dilute suspension or 'phase' of particles may be formed above the dense 'phase' of which the bed is composed and 'vaporization' or 'condensation' may take place between the phases These examples of behaviour suffice to illustrate the resemblance between non-homogeneous suspensions such as these and true liquids and gases The analogy, which was recognized by G MARTIN in 1928[1], has led to the common use of the word 'fluidization' in describing dynamic particulate systems. Although fluidization has long been studied and applied in pneumatic transport of materials and in mineral dressing, greatest stimulation of interest has occurred within the last decade because of the successful use of fluidized catalysts in cracking petroleum. The literature of fluidization has been expanded considerably within the last three or four years with emphasis placed upon design aspects and initial consideration of mechanisms A major symposium on the subject 'Dynamics of Fluid/Solid Systems' was held in December 1948[2] A tentative list of terms and definitions used to describe the more important stages of behaviour in fluid/solid systems has been proposed[3]

PRESSURE GRADIENT/BED EXPANSION/FLUID VELOCITY RELATIONSHIPS

The pressure gradient and extent of expansion of a mass of particles depend upon the velocity of the fluid through the mass These variables of state for particulate systems may be considered the counterparts of pressure, volume and temperature for true fluids Inter-relationships between the fluidizing variables may best be illustrated by means of non-circulating bed behaviour When solid material is circulated through the bed, as in certain industrial processes, the solid rate introduces an additional degree of freedom However, both circulating and non-circulating modes of operation deserve discussion

Non-circulating fluidized bed— A simple apparatus for measuring pressure gradient, bed expansion and fluid velocity properties is illustrated in *Figure 1* It consists of a glass tube provided with a metal screen to support the bed of particles An experiment is performed by causing a metered stream of gas or liquid to flow upwardly through the bed, fluid pressure drop being measured by means of appropriate manometers The extent of bed expansion is obtained simultaneously through measurement of the vertical position of the upper interface of the bed When this measurement is experimentally difficult to obtain the effective height of bed may be determined through static pressure measurements at different height positions of the bed of particles An extrapolation of these pressure/position measurements to the static pressure existing directly above the bed leads to the determination of the effective bed height

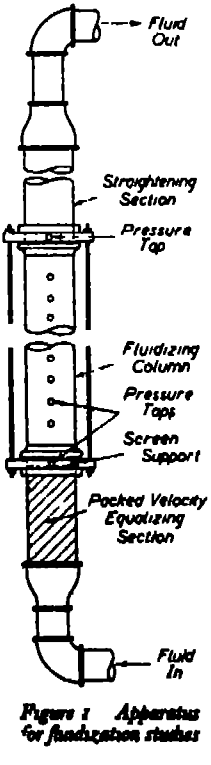

Figure 1 Apparatus for fluidization studies

Typical relationships between the three variables of interest are given for a bed of uniform particles in *Figure 2* In *Figure 2a* the logarithm of the pressure gradient, $\Delta P/L_1$, based upon total mass of solids (or initial height L_1) is related to the logarithm of u_0, the average linear fluid velocity based upon the empty tube area. *Figure 2b* shows the simultaneous variation of the logarithms of the fraction void ε with the logarithm of the velocity The fraction void is defined as $(V - V_s)/V$, where V is the total volume of the bed and V_s the volume of the solid particles Values of ε may vary between zero and unity as ultimate limits The stages of behaviour represented in *Figure 2* include a fixed bed at low velocities, a transition velocity and a fluidized bed at higher velocities The fixed bed regime exists from *A* to *C* A strong variation of pressure gradient with velocity is noted, but the fraction void is substantially constant Condition *C* marks the transition At velocities higher than *C* the bed is fluidized and a large bed expansion takes place at constant pressure gradient The transition at *C* between fixed and fluidized beds at a definite velocity is, in a sense, analogous to a phase transition from solid to fluid phase at a definite temperature

A fixed bed is simply a body of solid particles supported by direct contact with each other and the retaining walls The pressure gradient in fixed beds has been much studied and varies exponentially with velocity, as is evident from the linearity of *AB* in *Figure 2a* Deviation from linearity from *B* to *C* is characteristic of movement and readjustment of the particles in the bed to offer the largest possible free cross sectional area to flow The extent of the adjustments depends upon the degree of initial consolidation of the bed and may be quite large for powdered materials

Fixed bed behaviour terminates at the fluidizing velocity *C* At this point the bed begins to become mobile and colonies of particles remain continuously in motion Initially only part of the bed may be fluidized, the proportion of the bed in motion increasing rapidly as velocity is increased A slight drop in pressure as from *C* to *D* frequently takes place as the bed becomes dynamic The non-reproducibility of this pressure dip suggests that static friction is being overcome At the fluidizing point, within ordinary experimental precision, a balance is achieved between the fluid friction pressure drop and the net weight of the bed, which is the fraction of solids in the bed multiplied by the density difference between solid and fluid. However if the ratio of bed length to diameter is large, then forces acting upon the tube walls also enter significantly into the force equation.

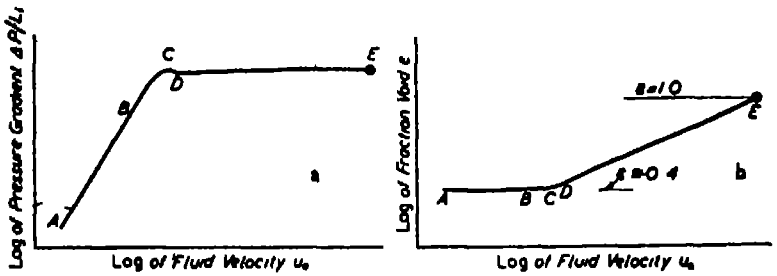

Figure 2 Typical relationships for fluidized beds consisting of uniform, non-agglomerating particles a *pressure gradient/fluid velocity* b *fraction void/fluid velocity*

Bed expansion during fluidization as from *D* to *E* has been found by several investigators to be approximately linear on a double logarithmic plot of ε versus u_0 as shown in *Figure 2b* The empirical expansion relation is thus exponential in form For example, R H WILHELM and M KWAUK[4] found this relationship to hold for fluidization in water of sand, glass beads, lead shot and *Socony* catalyst beads over a particle size range from 0 011 to 0 21 in (0 28 to 5 33 mm) diam With these relatively coarse particles it was found that the limit of expansion at $\varepsilon = 1$ occurred at the terminal velocity of fall of the individual particles Terminal conditions are shown in *Figure 2* by the closed point at *E* W K LEWIS, E R GILLILAND and W C BAUER[5] found a similar exponential expansion for glass spheres fluidized in air Particle sizes were from 0 0016 to 0 0061 in (0 41 to 0 16 mm) diam Experiments were terminated considerably short of the free fall velocity because of the high degree of turbulence and 'boiling' which is characteristic of solid/gas systems at high gas velocities, Nevertheless for coarse particles the ε/u_0 data were extrapolated satisfactorily to the individual terminal velocity However, for the very small particles the curve was extrapolated to a velocity several times the predicted value, suggesting particle agglomeration

Especially in systems fluidized by gases there is a tendency for particles to escape from the fluidized bed and to form a dilute suspension of particles above the bed This is particularly true for beds of non-uniform particle sizes M LEVA[6] has reported on the elutriation of fine particles from such mixed sizes. He found that an equilibrium exists between the concentration of fine particles in dilute and dense phases, the ratio being expressible by a modification of Henry's law for gas/liquid equilibria

Circulating fluidized bed— Circulating fluidized beds are used industrially in catalytic cracking units and in chemical reactors In this method of operating a constant level of dense phase fluidized catalyst is maintained Reactant gas is blown through the bed and catalyst solids are withdrawn from and recycled to the bed. Catalysts are selected non-uniform in particle size in order to favour the quality of fluidization and generally are encountered in the size range from about 10 to 100 μ Particle entrainment is an important operating consideration in these reactors As gas velocity through the bed is increased the solid concentration in the disperse phase increases while that of the dense phase decreases Ultimately, entrainment is total and a single disperse phase is obtained It is interesting that the velocity at which this occurs is substantially above that predictable from Stokes' law for individual particles, this again suggests that small particles tend to agglomerate during fluidization

Lewis, Gilliland and Bauer have measured fluid bed densities in a circulating system at different solid and gas rates The test section of their equipment consisted of 10 ft (3 m) of 1¼ in (3 2 cm) internal diameter brass tubing Glass beads were introduced in the bottom of the section together with the fluidizing air A cyclone separator at the top permitted return of entrained disperse phase to a solid feed standpipe *Figure 3* shows curves for glass beads 0 0016 (0 41 mm) diam The fraction void ε (inverse of bed density) is related to the solid feed rate at three gas flow rates Unstable operation was encountered at certain combinations of the prime feed rates and the limits of stable operation are indicated In general, the fraction void was inversely proportional to the solid feed rate at a given gas velocity and increased with

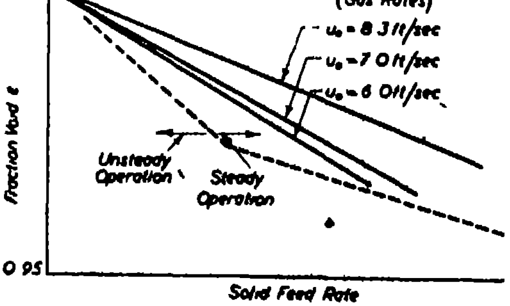

Figure 3 Interrelation of fraction void, solid and gas feed rates in circulating fluidized beds

increasing fluid velocity for a given feed rate. The beds were highly dilute compared with those obtained in non-circulating operation or those achieved in industrial practice.

Recent studies of a circulating system by S VALENTINE[7] in the author's laboratory dealt with the behaviour of large particles in an air stream. An interesting relationship between pneumatic transport and fluid bed formation was observed Essentials of the apparatus are illustrated in *Figure 4* A 4 in (10 2 cm) glass tube was fitted with side ports to permit introduction of a stream of particles and of air. Particles left the system either through an overhead bend in the pipe or by moving downward, accumulating in the collection leg *3* Slide valves were provided to measure particle population in sections *1* or *2* in order to compute the fraction void. Clay spheres, three sizes within the range 0 24 to 0 36 in (6 1 to 9·2 mm) diam, were used Interdependencies of fraction void, pressure drop and gas velocity at a single solid feed rate are illustrated in *Figure 5* Parametric curves for operation at other solid feed rates have been omitted Fractions void varied between 0 94 and 0 995 and gas velocity varied between 0 and 90 ft/sec (0 and 27·4 m/sec).

At highest air velocities, *A*, all particles were transported upward and out of the equipment Particle population in section *1* was sparse and did not vary greatly with fluid velocity changes Pressure drop through the section was primarily that due to fluid friction in the empty pipe There was co-current flow of gas and particles As air velocity was decreased to condition *B* an increase in particle population took place in section *1*, solid and air continuing to flow through the section At one point the particles were seen visibly to collect and fall abruptly as an accumulated group from upper section *1* of the apparatus to lower section *2*. Thereafter, at lower velocities than this critical value, the movement of particles was downward in countercurrent flow to the air A relatively high particle density was immediately formed in section *2*, *Figure 4*, at condition *C* in *Figure 5* Bubble formation and an upper interface were visible in the resulting bed of particles The critical zone is so labelled because in changing from co-current to countercurrent flow, events occurred more rapidly than could be measured readily The events take place under conditions of rapid acceleration A minimum in bed voidage (or maximum in density) was measured at *D*, at a velocity less than the suspending velocity for individual particles. As velocity was decreased further towards *E* the bed through which the descending stream of particles was now passing decreased markedly in particle content as shown by the rising fraction void curve The entire sequence of events was reversible. Stage *D* for different solid flow rates and particle sizes was shown to have identical expansion properties compared with non-circulating fluidized beds of the type illustrated in *Figure 2b* Thus on the basis of observation and quantitative comparison a

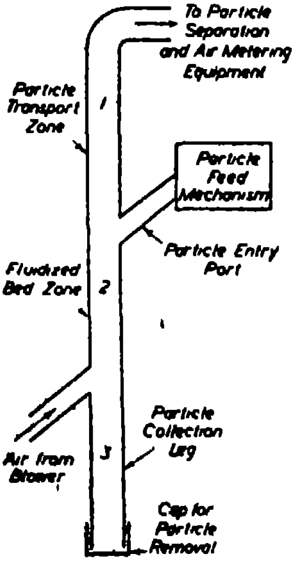

Figure 4. Apparatus for studying pneumatic transport/fluidized bed relationships

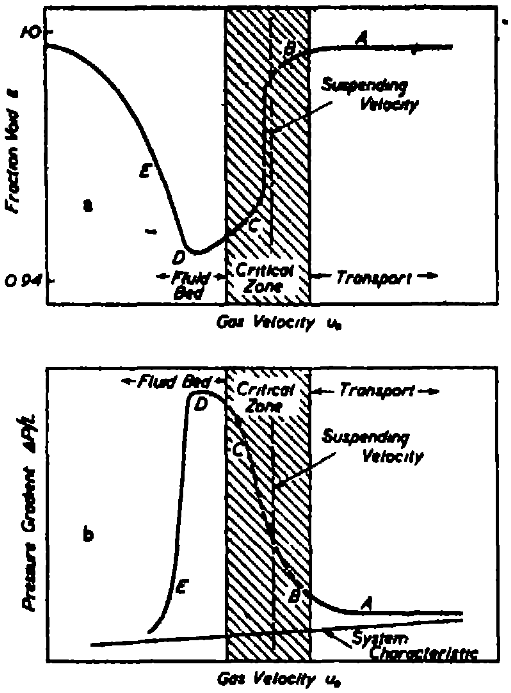

Figure 5 a fraction void/gas velocity and b pressure gradient/gas velocity variations during changes from particle transport to fluidized bed formation Operation at constant solid feed rate fluidized bed was formed as a transition state between co-current upward pneumatic transport and counter-current downward fall of particles

QUALITY OF FLUIDIZATION

The quality of fluidization is important The uniformity of temperature, concentration and particle/fluid contact in chemical reactors, for example, depends upon it Improper fluidization, on the other hand, may cause severe difficulties in reactor operation such as intense vibration of the entire structure due to excessive boiling and slugging action in which tons of material are tossed about

Extremes of quality—Extremes of quality have been observed and described by R H WILHELM and M KWAUK[4] The most uniform type of behaviour has been named particulate fluidization and is most commonly associated with fluidization by means of a liquid It is characterized by a progressive separation of the particles in a bed as fluid velocity is increased Individual particles move about with random motion and although there may be some circulation of masses of particles through the bed motion is primarily associated with the turbulent actions of individual particles In a bed of uniform particles dispersal is rather uniform throughout the suspending fluid A sharp upper interface is observed between the fluidized bed and clear fluid above it As fluid velocity is increased the bed structure is found to expand uniformly and an equable distribution of suspending fluid occurs throughout the bed cross section An upper equilibrium velocity exists at which the bed is vastly expanded and particles behave dynamically as individuals, unaffected by neighbouring particles This velocity is the normal terminal or free fall velocity

The other extreme of quality, aggregative fluidization, involves a high degree of segregation or non-uniformity of distribution between particles and suspending fluid It is most frequently encountered with a gas as the fluidizing medium In this type of fluidization the particles tend to remain close to each other, and whereas some of the fluid filters between particles much of it passes through the bed in the form of bubbles or pockets in the manner of gas bubbles rising through water Such pseudo-liquid beds are frequently referred to as 'boiling beds'. Turbulent motion is developed in the mass of particles and the apparent scale of turbulence appears to be about the size of the bubbles An increase in fluid velocity through the bed leads to an increase in the intensity of turbulent action. In a vessel of given size the scale and intensity may become sufficiently great at high fluid velocities to require cessation of operation because of instability The boundary zone at the free upper surface of a bed in aggregative fluidization generally is diffuse, as is the surface of a boiling liquid. A 'disperse phase' may appear above the more dense fluidized bed In a sense, the bubbles or regions of low particle density may also be thought of as 'disperse phase'.

When bubbles collect and increase in size until they are as large as the containing vessel an undesirable condition known as slug flow occurs Solid material is trapped between succeeding pockets of fluids and upward motion is in a piston-like manner Simultaneously the underside of each slug of solids may crumble and fall through the pocket below it

R D MORSE[8] suggested a quality scale based upon particulate and aggregative fluidization as extremes, intermediate qualities to vary with the extent of point differences in particle concentrations and in suspending fluid velocities For example, a bed in which fluid bubbles remain small and well distributed and in which a steady, smooth boiling action takes place may be considered intermediate in quality In a catalytic reactor such a bed may be optimum between the requirements of uniform chemical contacting between fluid and solid, and of turbulent mixing to control temperature.

Theory and criteria—Two complementary contributions by M MORSE and G L MATHESON, W A HERBST and P A HOLT[9] have provided the most satisfactory theory and criteria for the quality of fluidization presented to date A balance is postulated between *1* the segregation tendency or rate of separation of fluid from particles to form bubbles or pockets, and *2* the remixing tendency, or rate of gravity flow of particles into the pockets. Aggregative fluidization results from a high segregation rate of a free flowing material and particulate fluidization, from a low segregation rate and similar material A material with low fluidity causes poor fluidization Colonies of inactivity tend to form through flocculation of particles and in the limit a non-active bed is formed with fluid coursing through channels, as described by J D PARENT, N YAGOL and C S. STEINER[10]

The segregation tendency was treated by Morse as a fluid flow problem by applying the Carman-Kozeny equation[11] for flow through fixed packed beds to adjacent zones in a fluidised bed. The resulting equation indicated that segregation is self accelerating and is greater in deeper beds Segregation is favoured also by large particle size and density, by large differences in density between particle and fluid and by small fluid viscosity

These theoretical predictions are in accordance with the experimental findings Gas/solid systems with large density differences fluidize predominantly in the aggregative manner and smaller particle sizes lead to a smoother quality of fluidization although modified bubbling almost always persists Liquid/fluidized beds, which possess high fluid viscosity and lower density differences, commonly have low segregation rates characteristic of particulate fluidization However, with large, heavy particles, such as 0 11 in (2 8 mm) lead shot, it is possible to achieve a high segregation rate with clearly formed water bubbles rising through the bed to burst at the surface in a splash of lead shot

Matheson, Herbst and Holt measured relative viscosities of cracking catalysts, sand and metal oxides in a Stormer rotating viscosimeter Fluidizing air was provided during viscosity measurements It was found for narrow size cuts that viscosity decreased with particle size and possibly reached a minimum value because of particle flocculation below about 35 μ Spherical particles were more viscous than irregular particles Higher density of particle served to increase viscosity Proper particle size distribution has long been used to control quality of fluidization The authors demonstrated the strong effect of adding fine particles to a coarse cut in order to reduce the viscosity of the latter After a critical amount of fine material, thirty per cent, had been added, succeeding amounts were found to have small additional effect, particle interlocking presumably having been overcome The amount of gas a catalyst might hold between settled and expanded conditions in a fixed bed was found to affect the quality of fluidization favourably and the Stormer viscosity in an inverse manner Bed expansions as high as fifty per cent were reported Viscosity was theoretically found to be a function of the volume within which a particle can move freely in the more dense parts of a fluidized bed

DATA AND CORRELATIONS

Data— The quantitative experimental literature in fluidization is a relatively small body of knowledge The subjects reported upon have been fluid flow, heat transfer, mixing, particle/fluid mass transfer, particle transport and chemical kinetics in fluidized reactors The qualitative literature describing applications of fluidization in industrial processes is more extensive and will not be discussed

Papers by three groups of investigators have recorded sufficiently complete laboratory fluidization data to be suitable for fluid flow analyses R. H WILHELM and M KWAUK studied the fluidization characteristics of sand, glass beads, lead shot, crushed stone and *Socony* catalyst beads in water and air Particle size range was from 0 011 to 0 21 in (0 28 to 5·3 mm) M LEVA, M GRUMMER, M WEINTRAUB and M POLLCHIK and H H. STORCH[11-13] fluidized and measured the properties of 0 015 to 0 0020 in (0 38 to 0 05 mm) sand, 320 to 325 mesh iron Fischer-Tropsch catalyst and anthracite coal in air, carbon dioxide and helium W K LEWIS, E. R GILLILAND and W C BAUER[8] performed batch and circulating bed fluidization as well as hindered settling experiments Glass spheres, air and water were the materials used Particle sizes were between 0 022 and 0 0016 in (5 64 to 0 41 mm) diam

Turbulent mixing is important in achieving uniform bed temperatures It is related also to the mechanisms of heat transfer in fluidized beds E R GILLILAND and E A MASON[14] made exploratory measurements, with fluidized cracking catalyst in air, of the extent of mixing in the gas phase and among the particles A rough value for the gaseous eddy diffusion coefficient was determined through a helium injection technique The mixing of solids was determined indirectly by means of a divided heat transfer apparatus and was found to be sufficiently great to give essentially constant temperature throughout the apparatus R J MCCARTER, L F STUTZMAN and H A KOCH[15] presented a theory and preliminary results of eddy diffusion measurements involving the introduction of a point source of heat into a fluidized bed Heat flow results from container wall to fluidized beds of sand and Fischer-Tropsch iron catalyst in the size range of 100 to 400 mesh were reported by M LEVA, M WEINTRAUB and M GRUMMER[16] H S MICKLEY and C A TRILLING[17] measured heat transfer rates in circulating fluidized beds using external and internal heat sources Glass beads from 0 002 to 0 02 in (0 05 to 0 5 mm) diam and air were employed Transfer coefficients were found to be from three to seventy times greater than would be predicted if no particles had been present

Mass transfer from the particle to the fluid is a component mechanism in catalytic processes and in leaching or adsorption operations Mass transfer was studied by W RESNICK and R R WHITE[18] by means of the vaporization of naphthalene particles fluidized in air Similar experiments in the liquid phase were reported by L K MCCUNE and R H WILHELM[19] who measured the rate of dissolution of fluidized 2-naphthol spheres and flakes and also studied fixed bed and single particle rates

The pneumatic transportation of solids, in which a disperse phase is formed, has been practiced for a long time Recent pressure drop studies in vertical and horizontal transport of solids include those of

O H Hariu and M C Molstad[20] and of L Farber[21] Countercurrent spray type contactors have been analysed by J C Elgin and H C Foust[22] as fluidized systems By this means contactor pressure drop characteristics are capable of estimation within satisfactory limits based upon independent batch fluidization measurements with solid particles Reaction rate studies in fluidized systems have been the subject of two publications Gasification of carbon by carbon dioxide was reported upon by W K Lewis, E R Gilliland and G T McBride[23] The same authors with W A Reed[24] measured and analysed the rate of the reaction of methane with copper oxide

Correlations— Correlations of data are useful because they permit close assembly of quantities of diverse information , with proper precautions they permit interpolation and extension of results They may also contribute to the interpretations of behaviour Correlations of the flow properties of fluidized beds have received particular attention The general procedure has been to relate pressure gradient, fluid velocity and fraction void by means of dimensionless groups embodying these variables Various alternate forms of friction factor f and Reynolds' number R_e or products of these groups, have been employed A major distinction between procedures is the manner in which the fraction void is treated For example, R H Wilhelm and M Kwauk employed fR_e^2 and R_e as prime variables for correlating data and introduced fraction void as plotted parametric curves The Carman-Kozeny equation for flow through packed beds has served as the basis of alternate correlations This equation is based upon the assumption that a granular bed is the equivalent to parallel channels The resulting friction factor includes within it the effect of fraction void expressed by the ratio $\varepsilon^3/(1 - \varepsilon)$ Morse and Lewis, Gilliland and Bauer used the Carman-Kozeny friction factor successfully Deviations from the correlation were interpreted by the first author in terms of fluidization quality

The entire series of papers by M Leva and his co-workers were based on an alternate treatment of the Carman-Kozeny equation A 'fluidization efficiency' was defined and used in interpreting quality of fluidization and heat transfer The term is special It is the difference between the fluidizing velocity and the velocity predicted by the Carman-Kozeny equation for a fixed bed at the pressure drop and fraction void of fluidization, divided by the fluidizing velocity S Ergun and A A Orning[25] extended the treatment of Carman-Kozeny, which was originally derived for viscous flow, to include the effects of turbulence through the inclusion of an appropriate term in the square of the velocity When applied to fluidized beds very satisfactory agreement with data resulted A criterion for quality also was proposed as viscosity times superficial velocity In the fields of sedimentation and mineral dressing, fraction void has been treated in the form of ε^n Lewis, Gilliland and Bauer found that $\varepsilon^{4.65}$ as a component of the friction factor provides close correlation for data from air and water supported fluidizations A theoretical study of the fluidized state from the standpoint of statistical mechanics has been reported by J Bowman[26] and promises to be a major advance in the field This theory is closely allied to the classical theory for the kinetics of non-ideal fluids and relates the important variables of fluidization

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Some Applications of Servomechanisms

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AUTOMATIC control systems have a common basic theory regardless of the physical quantity under control, thus the problem of controlling the position or speed of a mass is closely related to that of controlling the flow of liquid in a pipe The term servomechanism is generally applied to a special class of automatic control system in which the motion of a mass (the load) is controlled by a lightly loaded input shaft or voltage, and which is actuated by a signal depending upon the difference (the error) between actual and desired behaviours, or, more generally, upon a function of this error, its time derivatives and/or integrals

The increasing complexity of modern machines and processes has resulted in the replacement of manual by automatic operation in many systems where man's speed of response or his physical characteristics are no longer adequate In these systems servomechanisms are playing an increasingly important part. The main purpose of this paper is to consider briefly some of the basic applications of servo systems with particular emphasis on the problems of remote position control and analogue computing

It is not practicable in a short review article to include a theoretical background to the subject and reference should be made to some of the authoritative texts on the theory and design of servomechanisms which have been published[1-7] recently

TYPES OF SERVOMECHANISMS

It is convenient to classify servomechanisms according to:

1 operating characteristics *e g* on/off control, continuous proportional control, proportional plus integral control *etc*

2 the physical nature of elements in the system *e g.* hydraulic, electrohydraulic, electrical, electropneumatic *etc*

3 function *e g* the function of a servomechanism can be described in terms of the nature of the input signal and the controlled condition, in this connection A TUSTIN has introduced the terms displacement-displacement, displacement-velocity, velocity-velocity, *etc* systems

In addition it is sometimes useful to distinguish between systems in which the input signal is always constant (these may be called position regulators), systems in which the input signal is a predetermined function of time, and those in which the input signal is not predetermined Flow diagrams of three typical servomechanisms which illustrate these points are shown in *Figures 1, 2* and *3*

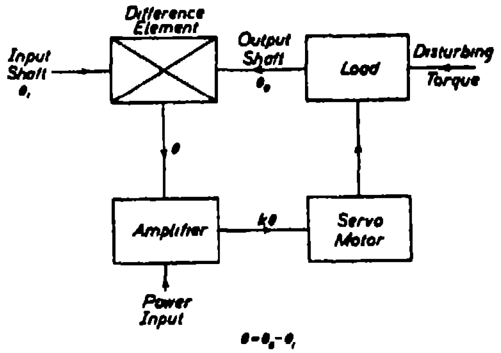

Figure 1 '*System A*' *Position control servomechanism* (*Displacement-displacement*)

System *A* represents a position control apparatus in which the position of the load (θ_o) is maintained approximately in correspondence with the position of the input shaft (θ_i) Alternatively the input signal may be defined by a direction in space—the bearing and angle of elevation of an aircraft with respect to a locator system for example—here the object of the control system is to point the locator at the target automatically Examples are automatic tracking radar systems and photoelectric tracking systems for positioning the image of a star on the slit of a spectrometer. Another interesting astronomical application arises in connection with the problem of

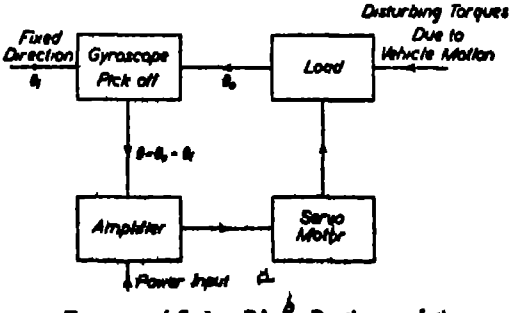

Figure 2. '*System B*', *Position regulating system.* (*On*[illegible])

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* Late of the Military College of Science, Shrivenham

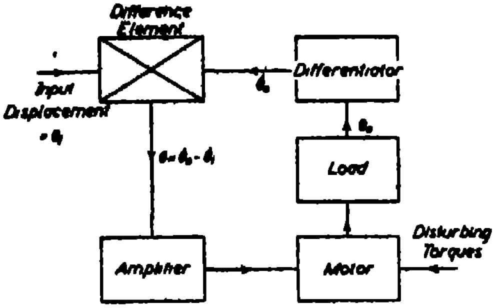

Figure 3 'System C' Speed regulating system (Displacement-velocity)

photographing the prominencies and corona of the sun's atmosphere by the creation of artificial eclipses[8] It is important to ensure that the image of the sun is accurately centred on the eclipsing disk so that intense light from the sun's surface does not reach the film, photoelectric cells detect any departure from normality and the direction in which the telescope is pointing is corrected by two servo motors actuated by the amplified error signals

An important feature of the above type of servomechanism is the fact that the disturbing torques acting on the load (non-linear friction, windage *etc*) can often be neglected and the motion of the input shaft can be regarded as the only disturbing influence, the input signal is generally a function of true time which is not predetermined

System *B* represents a position regulator where the load which it is desired to 'stabilize' is assumed to be part of a vehicle or craft, the problem is to ensure that the orientation of the load in space is unaffected by the angular motion of the vehicle or craft. An automatic aircraft pilot is a typical example of a stabilized system in which the roll, pitch, and yaw of the aircraft must be compensated The input signal is a fixed direction in space in this example and the roll, pitch, and yaw of the aircraft constitute the major disturbances which the position regulator must follow, albeit 180° out of phase, in order to stabilize the load As in the previous example this system must also handle disturbances which are true functions of time. But the design problem may be more severe than the design of a normal position control system because the disturbing functions may be more complex and more varied It is a mistake therefore to assume that regulation (of temperature, pressure, position *etc*) is a more straightforward problem than position control in which the input signal is continually varying

System *C* can be regarded either as a speed regulator, when the input signal θ_i is usually a constant and the main disturbances arise as a result of changes in load or power supply, or alternatively as an integrator (*i e* speed control system), when the input signal will probably vary but the effect of other extraneous disturbances is not so important

REMOTE POSITION CONTROL SYSTEMS

It frequently happens in practice that the controlled member (the load) is situated remotely with respect to the controlling member (the input shaft) If the former is a simple pointer or index and the object of the control system is merely to provide a remote indication of the behaviour of the input shaft, the problem is readily solved by utilizing the *Magslip* indication system[9], which is essentially a data transmission system But if the controlled member is a large mass we need, in addition, a torque amplifier system For example, the direction in which an anti-aircraft gun points is often controlled by a computing system which is normally housed in a control room situated some distance from the actual gun mounting Moreover, in the manipulation of the controls associated with atomic piles or in the associated chemical separation processes, it is impracticable to introduce local manual controls; in these instances automatic remote position controls provide the only solution

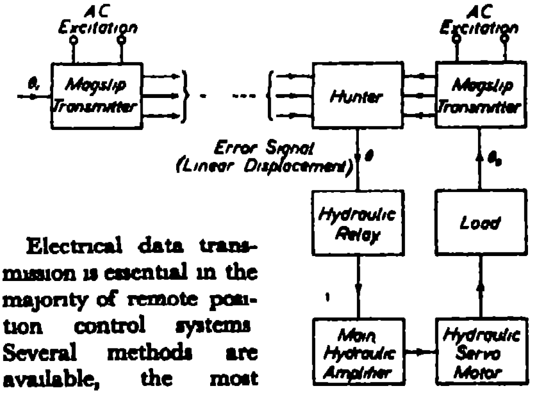

Figure 4 Hydraulic remote position control system

Electrical data transmission is essential in the majority of remote position control systems Several methods are available, the most common including the application of accurate direct current (*DC*) potentiometers, and the *Magslip* system—a roughly equivalent type is the *Selsyn* or *Synchro* system In most applications the *Magslip* (or *Synchro*) type system is preferred because it satisfies the two requirements of accuracy and low power level transmission, and in addition several remote loads can be controlled from a single transmitter without appreciable loss of accuracy There are two basic methods of using this system, illustrated in *Figures 4* and *5*[9].

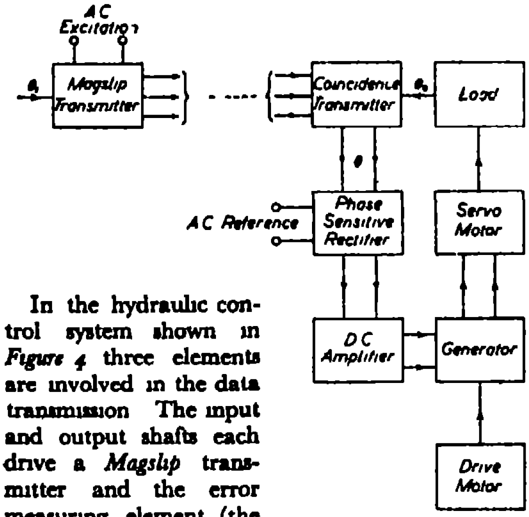

Figure 5 *Electrical remote position control system*

In the hydraulic control system shown in *Figure 4* three elements are involved in the data transmission The input and output shafts each drive a *Magslip* transmitter and the error measuring element (the 'Hunter'), which is actuated by them, can be regarded as the electrical equivalent of a mechanical differential gear The error signal appears as an angular rotation of the hunter rotor, from a zero position corresponding to zero error, and this normally displaces the small pilot valve of a hydraulic relay which in turn controls the flow of oil to the main hydraulic amplifier and thence to the hydraulic servo motor

In the electrical servo system shown in *Figure 5*, only two elements are involved in the error measuring process A standard transmitter is driven by the input shaft and its stator windings are connected to the equivalent windings of the so-called coincidence transmitter (in the U S A this element is analogous to the 'synchro control transformer') which is oriented initially so that when input and output shafts are in alignment, the voltage induced in the rotor windings of the latter is zero If, subsequently, the input shaft is rotated through a small angle, say ± 20°, an alternating current (*AC*) signal, in phase or 180° out of phase (depending on the sign of the error) with the supply voltage, is induced in the rotor winding of the coincidence transmitter, the root mean square value of this signal is proportional to the error This error signal is usually rectified by a 'phase-sensitive rectifier' and the resulting *DC* signal is amplified and applied either to the field windings of a Ward-Leonard, *Metadyne*, or *Amplidyne* generator, or to the field windings of a *DC* motor with constant armature excitation This procedure only applies to essentially *DC* servo systems and is modified when the servo motor is an *AC* induction motor for example

If it is required to control the position of the load very accurately so that, for example, the maximum error under dynamic conditions does not exceed 2 or 3 minutes of arc the systems described above are inadequate, chiefly because the average error of the *Magslip* system is already of the order of 15–30 minutes of arc The most convenient method of overcoming this difficulty is to introduce 'coarse' and 'fine' data transmission systems, the former ensures that the input and output members are always in the same sector (the sector value is $360/N$ degrees where N is the value of the gear ratio between coarse and fine transmitters) and the 'fine' channel handles the main control operations An automatic switch changes from 'coarse' to 'fine' control when the magnitude of the error is decreasing and reaches a certain value, and *vice versa* when the error increases beyond the same limiting value Clearly, assuming ideal gearing, the accuracy of the data transmission and error measurement can be increased by a factor of N compared with the 'coarse' channel acting alone, N is usually of the order of 18, or sometimes 36 The principle of the method is illustrated in *Figure 6*

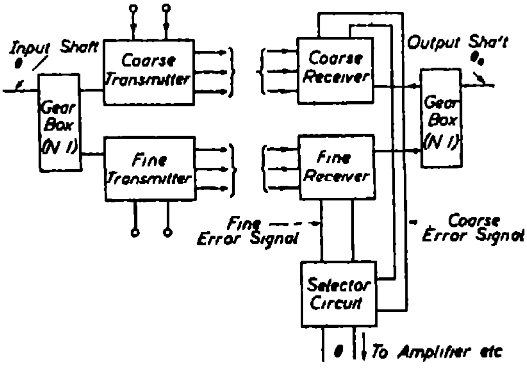

Figure 6 *Principle of 'coarse' and 'fine' transmission*

In the design of servo systems it is necessary to pay special attention to the problem of obtaining well damped behaviour when the system is subjected to sudden disturbances The hydraulic servo system considered briefly above is not usually difficult to stabilize, especially if the speed of response of the error-measuring element (the hunter) is increased by introducing centring springs, because the time constants of hydraulic relay, amplifier and motor are generally small On the other hand in order to achieve adequate damping in the response of electrical servos it is often necessary to introduce 'derivative of error' networks or 'output velocity and/or acceleration' feedback, these special techniques are not indicated in the flow diagram and a discussion of them is beyond the scope of this paper

Notwithstanding appreciable improvements in the design of mechanical and electrical components, the accuracy of remote position control systems and indeed of all servomechanisms will always be limited by two basic factors First, a servomechanism is essentially an analogue device and the accuracy of the system is ultimately limited by the accuracy with which mechanical parts can be machined, the accuracy of winding potentiometers, and so on For example, the accuracy of measurement of linear and angular misalignments cannot be greatly improved over and above that obtainable at present, but it is probable that the deleterious effects of backlash and non-linear friction will be reduced appreciably by improved gear cutting processes and lubrication Secondly, all continuous error-actuated servo systems must possess inherent dynamic following errors, although in practice it is possible to eliminate dynamic lags which depend on the velocity of the output member, it is quite impracticable to eliminate acceleration lags completely unless we are prepared to tolerate very oscillatory transient behaviour of the system On the other hand dynamic lags may be compensated by feed-forward of the first and perhaps of the second time derivatives of the input shaft displacement

ANALOGUE COMPUTORS

Some of the most elegant applications of servomechanisms arise in the design of analogue computing systems[10], three important examples are

1. torque amplifiers and remote position control systems in the differential analyser,
2. the application of servomechanisms in carrying out simple arithmetical operations automatically, and in the solution of simple equations,
3. electromechanical integrators e g the *Velodyne* system

We will consider each of these applications in turn

Differential analyser—The importance of servomechanisms in the design of the differential analyser cannot be over-emphasized, indeed recent designs are based almost entirely on the types of servo systems which are used For example, the original Bush machine[11] and most of the machines based on it incorporate the mechanical capstan-type torque-amplifiers, and as a direct consequence it is necessary to transmit data from one unit to another by interconnecting the units mechanically through a large flexible gearbox. Subsequently V BUSH and S H CALDWELL[12] decided to replace the mechanical torque-amplifiers by a specially designed electrical remote position control system, by means of which the output of any one unit can control the input of one or more units by making appropriate connections through an automatic telephone switchboard This decision completely changed the whole basis of design of the new differential analyser at the Massachusetts Institute of Technology and resulted in a far more flexible and effective machine for the solution of ordinary differential equations

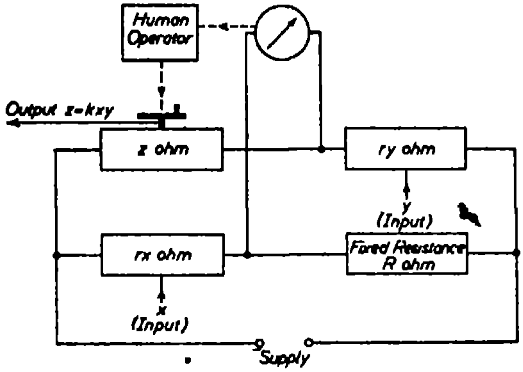

Figure 7 Manually controlled 'bridge multiplier'

Multiplication and division—Analogue methods of carrying out arithmetical operations are often appreciably facilitated by introducing servomechanisms Consider as a simple example the well known 'bridge' method of multiplying or dividing two quantities x and y which may be varying continually In the system shown in *Figure 7* a human operator rotates the handwheel z so that the galvanometer deflection is always zero, the handwheel displacement z is then given by

$$z = r^2xy/R = kxy$$

But if x and y vary fairly rapidly the effect of human

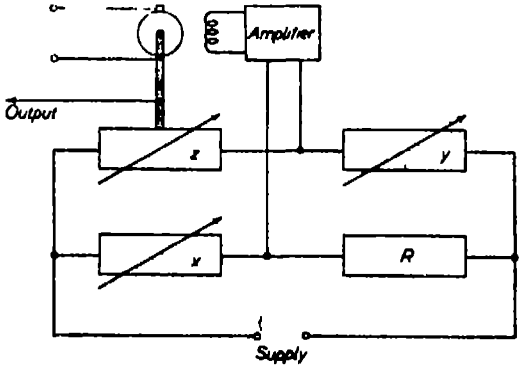

Figure 8 Automatic 'bridge multiplier'

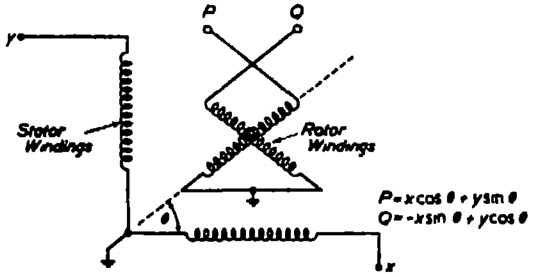

Figure 9 *Diagrammatic representation of Magslip resolver*

reaction time may cause large errors in the value of the product. The introduction of a high speed servomechanism as indicated in *Figure 8* will usually improve the accuracy of the process and at the same time relieve the human operator of an exacting and probably boring task.

If the fixed resistance R and the variable resistance (ry) are interchanged the system will generate a quotient z:

$$z = Rx/y$$

Solution of equations— In addition to the large and elaborate analogue computing machines, such as the differential analyser, many small scale computors have been developed for the solution of special problems. The continuous conversion of cartesian to polar coordinates is a typical example: given (x,y) to determine instrumentally (r, θ). There are several ways of solving the equations

$$x \cos\theta + y \sin\theta = r$$
$$-x \sin\theta + y \cos\theta = 0$$

which relate cartesians to polars in two dimensions.

Suppose x and y are given in the form of AC voltages and r is required as a voltage and θ as an angular displacement of a shaft. One of the most convenient methods of solving the above equations is by using a 'Magslip resolver'[16] with 'crossed rotor windings', this unit has two stator windings, to which are applied voltages x and y respectively, which produce magnetic fields at right angles, and two mutually perpendicular rotor windings. The unit can be represented schematically as shown in *Figure 9*. Referring to this diagram, suppose we rotate the rotor of the resolver, so that $P = 0$, then θ is the angle of rotation with respect to the fixed reference axis, and $Q = r$ volts gives the desired linear coordinate. The process can clearly be carried out automatically by introducing a servomechanism, and *Figure 10* shows a flow diagram of the automatic coordinate converter.

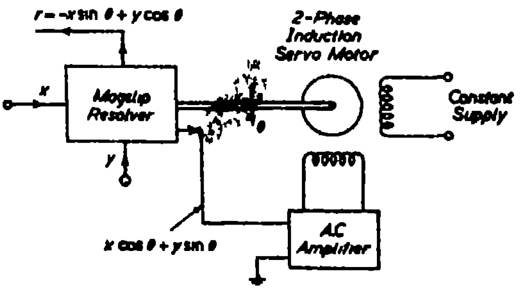

Figure 10 *Automatic converter for transforming Cartesian to polar coordinates*

Servo systems as integrators— All servomechanisms which are classified as displacement-velocity systems can be regarded as integrators although few are used as such. One of the most successful 'servo integrators' which has been used extensively in analogue computors and which provides the basis of an electromechanical differential analyser is the *Velodyne*[14, 15] system shown schematically in *Figure 11*.

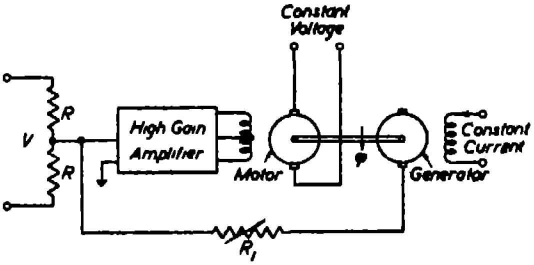

Figure 11 *The Velodyne integrator.*

The servo motor and generator are assembled as a single machine with suitable shielding to minimize interaction between the two component machines. Assuming very high amplification and negligible time constant of the motor field winding and generator armature winding, the relationship between V and φ can be written

$$\varphi = k \int V\,dt$$

in which k, the integrator constant, can be varied by varying the resistance R_1. The speed range of these integrators may be as high as 1,000 : 1 and their accuracy certainly compares favourably with the ball and disk type integrators normally used in fire control computing equipment.

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Livestock Breeding Research

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HISTORY AND ORGANIZATION

ANIMAL breeding is the process of artificially selecting those animals of the colony or herd to be used for reproduction, deciding which males are to be mated with which females, and controlling the physiological processes of reproduction as far as it may be necessary or desirable The aim of livestock breeding research is to reveal methods by which farm animals may be genetically improved The application of the results obtained is the function of the educational and advisory services, of the government agricultural departments, and of the pedigree breeders and their organizations

In the past this division of labour did not exist The men who bred the animals were both their improvers and their commercial exploiters Empirically they discovered the methods to use, and the good effects with which they applied them are witnessed today by the many improved breeds of livestock in Europe and America

The rediscovery of mendelism in 1900 gave rise to hopes that livestock improvement would henceforth be firmly based on the new science of genetics These hopes were too optimistic Mendelism was able to explain the mode of inheritance of horns and coat colour which are usually due to simple genes , it made possible the production of autosexing breeds of poultry and it could help in the avoidance of monsters and abnormalities due to simple recessive genes But mendelian genetics was quite unable to help in the improvement of meat, milk or egg production : these are all quantitative or polygenic characters The young science of biometry, founded by F. GALTON and K PEARSON, was a suitable instrument for their study but mendelism was espoused by W BATESON and R C PUNNETT and became the official creed of British genetics

The result was that during the first thirty years of the twentieth century livestock breeding research in Britain consisted only of *1* analyses of simple genetic situations which had little economic importance, *2* unsuccessful attempts to force quantitative characters into the mendelian mould by experiments designed to determine the number of genes controlling them, and *3* *ad hoc* trials of current breeding practices *e g* experiments to determine the most suitable breeds to cross for specific purposes During the same period important pioneer work was done in Edinburgh and Cambridge on the physiology of growth and reproduction in farm animals, described by F H A MARSHALL and J HAMMOND[1]

During the 1939–45 war, which focused attention on methods of increasing home food supplies, the Agricultural Research Council (A R C) realized how small was the volume of research in Britain on the genetical improvement of food producing animals Individual research workers at universities and other research institutions can conveniently carry out research on small laboratory animals Farm animals of large size, slow breeding habit and commercial value (especially cattle) need outlays of space, time and money which only a large scale public organization can afford Accordingly, following a thorough exploration of the whole subject, the A R C decided to organize its own animal breeding research institutes In 1945 the Animal Breeding and Genetics Research Organization (A B G R.O) was set up with R G WHITE as director Its headquarters were established in Edinburgh which was already the seat of the only Institute of Animal Genetics in the country—an institute which had earned a world wide reputation under its first director, F A. E CREW In 1947 C. H. WADDINGTON, the chief geneticist of A.B.G R O, was appointed

Professor of Animal Genetics in the University of Edinburgh and the Genetics Laboratory of A B G R O was housed in the University Institute of Animal Genetics Thus continuity of work was maintained between the new organization and the old[2]

A parallel development was the foundation in 1947, again by the A R C, of the Poultry Research Centre in Edinburgh with A W GREENWOOD as Director This centre will continue the work on poultry breeding and physiology begun in the Institute of Animal Genetics[3]

In the U S A a similar development of large central research organizations has occurred Each state has its Agricultural Experiment Station, many of these have important livestock breeding sections In addition the federal research organizations are increasing in number and importance The Bureau of Animal Industry and the Bureau of Dairy Industry of the U S Department of Agriculture carry out vast research programmes at the Agricultural Research Center, Beltsville, Maryland, and also at regional research laboratories The three concerned with animal breeding are the Regional Swine Breeding Laboratory with its headquarters at Ames, Iowa, the Range Livestock Experiment Station at Miles City, Montana (beef cattle), and the Western Sheep Breeding Laboratory at Dubois, Idaho[4-6]

METHODS

Mendelism has now settled down as one of the foundation stones of animal breeding, but it is only one and not the most important Research on the variation and inheritance of quantitative characters is now firmly based on the statistical methods developed by K PEARSON and R A FISHER and applied so fruitfully to genetics by J B S HALDANE and S WRIGHT and to livestock breeding by J L LUSH[7] The livestock geneticist is no longer concerned merely with the behaviour of single gene pairs, he is interested in the behaviour of populations of genes In short, livestock improvement has now become a question of increasing the proportions of desirable genes in the gene population represented by the herd, strain or breed

A few examples of methods and techniques will be given Inbreeding, the mating of animals more closely related than the average of the population from which they are taken, has always been an important tool of the breeder, but until S WRIGHT[8] tackled the problem no satisfactory method of measuring degrees of inbreeding had been suggested Wright showed how inbreeding could be measured by the rate of increase in homozygotic gene loci He developed the formula

$$F = \tfrac{1}{2}\Sigma\,(\tfrac{1}{2})^n(1 + F_A)$$

where F is the inbreeding coefficient (i e the percentage decrease in heterozygosis relative to the foundation stock) of any given individual, n is the number of generations between the dam, back to any common ancestor of sire and dam, and forward again to the sire, and F_A is the coefficient of inbreeding of the common ancestor This coefficient is now universally used as a measure of inbreeding Mating a sire to his daughter produces offspring which are 25 per cent inbred

In considering the variation of any character of economic importance the first question which needs an answer is how much of the variation is genetic and is therefore capable of transmission to the offspring, and how much is due solely to the environment? This proportion can be represented by a quantity called the 'heritability', which is defined as the ratio of the additive genetic variance, σ_G^2, to the total variance i e the sums of the genetic and environmental variance, $\sigma_G^2 + \sigma_E^2$

The argument between those who believe in 'nature' and the apostles of 'nurture' can now be resolved precisely for a particular characteristic of a given species For instance, many studies have indicated that the heritability of first lactation milk yield in cattle is about 0 25 i e of the variation in milk yield within a herd 75 per cent is due to environment and 25 per cent to heredity A striking illustration of the importance of the environment is provided by a recent Danish experiment[9] Ten cows from one of the best herds in the country were given individual attention and fed a highly appetizing protein rich diet The annual milk yield was nearly doubled and in 1948–49 the ten cows averaged 22,200 lb of milk, a truly amazing performance!

R W PHILLIPS[9, 10] lists estimates that have been made by American and Swedish workers of the heritability of various characters in beef and dairy cattle Heritability can be calculated either from the intra-sire regression of offspring on dams or from the correlation between half-sibs In the case of cattle it can also be obtained directly by comparing the behaviour of monozygotic identical twins under different treatments

The recent confirmation of the occurrence of monozygotic twins in cattle has, indeed, put a useful tool into the hands of the research worker Because of their identity of genotype all differences between them must be due to differences in environment Research on identical twins is proceeding in New Zealand, in Sweden[11] and in Great Britain

RESULTS

The field of livestock breeding research can be divided into three parts

1. examination of the time honoured methods of the breeder—those of selection, inbreeding, crossbreeding—in order to discover their biological mode of action and to refine their application to livestock improvement
2. study of the genetic nature of the livestock material available in the pedigree and commercial herds of the country and of the methods of breeding currently employed This has been called operational research
3. development of techniques to control the reproductive processes so that more material is available for the application of genetic methods of improvement

Selection— The basis of animal breeding is the selection of those animals which are to be the parents of the next generation The earlier the best animals can be chosen the quicker the rate of improvement Many studies have been undertaken attempting to establish a correlation between the appearance of an animal and its performance so that selection can be undertaken at an early age The results obtained with cattle have been carefully summarized by PHILLIPS[10] Three points emerge *a* it is not possible to estimate the milk yield of a cow from any of the ordinary points of conformation considered in judging cattle, *b* there is a small positive correlation between milk yield and body size, or any body measurement which can be considered an index of size, and *c* the milk characters (udder, milk veins, milk wells) may be of some use for estimating milk yield In this connection an important observation has been made[11] indicating that milk production may be predicted from the amount of glandular tissue (estimated by palpation) in the udder of the four months old calf

Meat conformation is more readily observable in animals of both sexes and all ages Nevertheless, the master breeders undoubtedly realized what mendelism later proved, namely that like does not necessarily breed like Or, as we should now put it, selection on phenotype is only satisfactory if heritability is high If the heritability is low or if the male does not exhibit the character (*e g* milk and egg production), selection of sires must be based on genotype Genotype cannot be directly measured but it can be evaluated from pedigree, from the performance of collateral relatives and from the performance of offspring This latter method is usually the most accurate method of determining a sire's breeding value However this does not mean that progeny testing will inevitably lead to a higher rate of genetic improvement per annum than selection on the basis of pedigree and performance The improvement per generation may be high but the interval between generations is increased by the time necessary for the results of the progeny test to appear G E DICKERSON and L N HAZEL[12] have shown that progeny testing will only increase the annual rate of genetic improvement if *1* waiting for the progeny test information does not unduly increase the generation interval, *2* the reproductive rate is low, and *3* the basis for making early selections is relatively inaccurate *i e* if heritability is low

Progeny testing of meat animals is still only at the stage of trying to define the best measures of productivity and the most accurate recording methods Indices being studied in the U S A include birth weight, weaning weight, rate of gain, economy of gain (*i e* efficiency of food utilization), slaughter weight and carcass characters The performance of dairy cattle, on the other hand, can be easily measured by milk yield and butterfat production Here current work is concerned with methods of applying the progeny test so that errors due to environmental variations are minimized For instance, should bulls be compared by *1* the average yield of their unselected daughters, *2* the average difference between the yields of these daughters and the yields of their dams, or *3* their average yield compared with the average yield of contemporaries in the herd[13] The last method appears to be the most satisfactory

In any discussion of selection the problem of the environmental conditions under which selection should be practised arises J HAMMOND[14] and A D BUCHANAN-SMITH[15] consider that selection should take place under conditions which are optimal for the character concerned This will bring out high production but it will neglect adaptation to environment The latter may be more important where the environment is unfavourable Years of experience have shown that high producing animals from temperate climates do not continue to produce well when taken to the tropics In this instance selection under the local poor conditions is the only way to obtain genetic improvement in performance An experiment to test these two views can be conveniently carried out on laboratory animals and such a test is at present under way in Edinburgh D S FALCONER of A B G R O is selecting mice for body weight at two levels of feeding

If selection for several characteristics is desired, progress will be most rapid if the characters are combined in a total score which is used as the basis of selection[16] This is much more efficient than selecting for each character separately in turn, or culling for each character independently L N HAZEL[17] explains the method of constructing such selection indices given the relative economic values of the traits, their standard deviations, the phenotypic and genetic correlations between them in pairs and their heritabilities

Inbreeding— Owing to religious prejudice and to the contradictory results obtained, the value of inbreeding for improving livestock is still a matter for heated controversy among breeders Its genetic effect is to increase the amount of homozygosity, it will, therefore, only have good results if more favourable than unfavourable genes are thus fixed in the inbred line Certainly many breeders have used inbreeding successfully On the other hand, since the tendency is for favourable genes to be dominant, the recessive genes, which are revealed by inbreeding, are more likely to be harmful than beneficial Extremely severe selection is essential to eliminate these recessives and thus avoid inbreeding degeneration Even so, of all lines started few will survive A ROBERTSON's summary[18] of three experiments on inbreeding dairy cattle in the U S A shows that out of thirteen lines started ten were discarded because of deleterious recessives and two more because of low milk yield All lines showed a decline in vigour, fertility and productivity

Likewise, in the extensive pig experiments under the U S Regional Swine Breeding Laboratory, inbreeding has been accompanied by a decline in vigour, fertility and performance[6, 19] At the Minnesota station, for instance, only four out of the original eleven lines survived During the second five years' work at this station, however, the decline in performance was avoided by starting with crossbred or crossinbred stock, by increasing the rigour of selection, and by keeping the degree of inbreeding below 30 to 40 per cent[20] In an inbreeding experiment with White Leghorn fowls M PEASE[21] records the same decline in productivity and the same petering out of inbred lines After five years of brother–sister mating only one out of the original twenty hens still survived

Crossing inbred lines— The spectacular results achieved with hybrid maize suggested that the contribution of inbreeding to livestock breeding might lie in the crossing of the inbred lines produced rather than in the fixing of desirable genes in the lines themselves But only 2 4 per cent of about 30,000 maize lines proved useful[6] and a stupendous number of crosses must have been made Consider the scale of a corresponding programme with cattle, or even with the more quickly multiplying pig or fowl !

Nevertheless a beginning has been made with pigs in the U S A., but the results are neither consistent nor conclusive R W PHILLIPS[6] concludes that 'crossing of inbred lines has usually corrected the decline in performance that accompanied inbreeding, and in some cases appears to result in a considerable increase over the performance of non-inbred stock' It has been confirmed[19, 20] that this improvement occurs with only some of the inbred lines and that the results are better if the inbred lines come from unrelated stock *e g* from different breeds

M PEASE[21] gives the results of crossing the five inbred lines of White Leghorns then available Production of the incrosses sometimes returned to the level of the outbred controls or even exceeded it. When the five lines were crossed reciprocally in all combinations except two, egg yield in forty four weeks was higher than in the outbred control flock in thirteen crosses and lower in five

Crossbreeding— These results indicate that there is some merit in heterosis, some real advantage in what has, until recently, been called hybrid vigour The appearance of this phenomenon when breeds of livestock are crossed has been sufficiently demonstrated by many experiments in which the crossbred progeny have shown themselves to be superior to the purebred parents Indeed crossbreeding on a commercial scale is a standard practice in all parts of the world and with all species of livestock but particularly in the production of fat lambs and beef cattle where rapid growth rate is a desideratum

Its mechanism is less clear and requires further fundamental research It should be noted that crossing of heterozygous breeds does not give hybrid vigour whereas crossing inbred lines from different breeds gives a maximum amount

The results of crossbreeding experiments with dairy cattle have been analysed[22] The evidence of hybrid vigour in butterfat production is, on the whole, uncertain and unreliable The inconclusiveness of these experiments can be attributed to three main facts *a* three quarters of the variation in milk yield is non-genetic in origin, *b* the genetic heterogeneity of the parent stocks leads to genetic variation in the F_1 generation, and *c* only a few proven sires were used so that high production in the F_1 might merely reflect the inheritance of individual merit. This last criticism applies particularly to a recent experiment at Beltsville, U S A

Investigations into the fundamental nature of heterosis are at present in progress in Edinburgh, and A B G R O is also planning experiments to detect the presence of the phenomenon when dairy cattle are crossed

Operational research— Apart from the strictly experimental research so far described much information can be obtained from the accumulated records of the breeding industry, usually by the application of statistical methods In Great Britain such records are of four kinds :

1 The herdbooks, which record little more than the pedigrees of registered animals Nevertheless they supply sufficient information for studies of population structure and vital statistics of the pedigree breeding material Such factors as herd size, herd duration, generation length, migration of breeding animals, degree of inbreeding in the breed, will all have a great influence on the rate of improvement possible by the application of genetic methods

2 The records of milk production kept by the Milk Marketing Boards are invaluable sources of material for the study of the genetics of milk and butterfat production

3 The records of artificial insemination centres, which deal almost entirely with dairy or dual purpose cattle Together with *2* these records offer the most fruitful opportunity for research

4 The Ministry of Food keeps records of all animals graded and slaughtered These should be a useful source of material for operational research on meat animals but, with the exception of an investigation on dual purpose cattle which A B G R O is just commencing, the figures taken at livestock grading centres are not at present being used in any large scale programme of research It must be borne in mind, however, that the sale of fat cattle and sheep according to weight and grade and the centralizing of their purchase in the Ministry of Food was a wartime innovation Furthermore, there is no central collecting and analysing agency analogous with the Milk Marketing Boards The world meat shortage and the increasing scarcity of dollar exchange should induce the organizations concerned to explore the possibilities of establishing some nation wide system of meat recording This would supply the information essential for research on and improvement of home meat production

Control of reproduction—The more quickly an animal reproduces the more rapidly can genetic improvement be effected Furthermore, the more widely a superior sire can be used and the more offspring a superior dam can produce in her lifetime the more quickly can their improved genotypes be distributed through a population Artificial insemination is a technique which has appealed to the farmer because it makes the management of his herd easier. Because it enables each good sire to father many more offspring it is of immense importance in genetic livestock improvement Its possibilities in this direction have not yet been exploited, but there are signs that the artificial insemination centres in England and Wales will soon be operating an extensive system of progeny testing for breeding their own bulls. The semen from the superior bulls thus detected will then be used on commercial herds and the process will lead to a slow but steady genetic improvement of dairy cattle

The corresponding technique applied to females—it might be called ' artificial in-ovation '—is still at the experimental stage Ova have been collected from female rabbits superovulated by the injection of gonadotropic hormone and transferred to other does to be successfully gestated In the case of cows the collection of ova is possible but the transferred ova have not yet been successfully grown in foster mothers

Another possibility which may have far reaching effects on livestock breeding is the control of the sex ratio, leading to the production of male or female offspring at will Considerable research has been done on this subject, especially in Russia and in the U S A , so far without the development of any successful technique

The stimulation of growth and fertility by hormonal treatment will not be discussed here since it is not included in the term ' breeding ' in its narrow sense Those interested will find accounts of recent work in the reviews[12-19]

Current research in livestock breeding in the United Kingdom has been summarized by J P MAULE[20] The U S Department of Agriculture Yearbook[21] gives semi-popular accounts of recent American work

CONCLUSION

In this short outline it has only been possible to touch on some of the topics which are being investigated in the field of livestock breeding research. It has been difficult to restrict discussion to research , questions of livestock improvement were continually coming into the picture That research and improvement should remain so inextricably mixed in spite of their administrative separation is an excellent sign

At the same time, although the emphasis has been on farm animals, it has been impossible entirely to ignore related work on laboratory animals Here again pure and applied research must, and do, go hand in hand Nowhere is that more conspicuous than in the Edinburgh organizations For example, if fundamental geneticists working on *Drosophila* succeed in developing a method of producing directed mutations, they may well confer greater benefits on the livestock industry than the workers in applied animal breeding.

The stock breeder must not, however, hope for immediate spectacular results. It may no longer be

Diffraction— The resolving power of an instrument is always limited by diffraction phenomena. When the aberrations i.e. distortions of the wave front, are small their effect on the diffraction pattern is practically negligible. It is then possible to give a new form to the Rayleigh limit and to obtain better precision by fixing a maximum to the mean square of the distortion of the wave front ($\lambda^2/180$) instead of a maximum to the distortion itself ($\lambda/4$) as in Lord RAYLEIGH's method. This can be applied to any aberration, especially to decentration effects. In fact this transformation of the Rayleigh limit does not enable us to know the complete structure of the diffraction pattern in the presence of an arbitrary aberration. This problem involves great mathematical difficulties and in order to avoid them a special machine has been constructed to perform the diffraction integrals in cases of classical aberrations. With that machine it is possible to calculate in advance the resolving power of a system as soon as the aberrations have been computed, the computer is then able to take account of diffraction when choosing the optimum correction of aberrations. Various industrial and research problems have already been solved with the machine.

The theoretical basis of diffraction phenomena has been studied and a critical study of the Huygens-Fresnel principle has been given recently by F CROZE and G DARMOIS[5], but the effect of perturbations on the propagation of light by the rim of the pupil is still unknown. Although experimental study of diffraction patterns has shown that it is negligible in most practical examples it is interesting to find the extent of those perturbations; experiments are now being made to obtain complete information on the subject.

Surface defects— The formation of the optical image can be also influenced by the presence of small accidental defects on the surfaces or in the glass. A systematic study has been undertaken by M FRANÇON and despite great experimental difficulties the exact effect of scratches on the glass surfaces on the diffraction pattern has been tested. It has been necessary to suppress the effect of the diffraction by the rims of the pupil by using a screen of a special shape, avoiding diffraction in a direction perpendicular to that of the scratch. It has been possible to define reasonable tolerances for the presence of random defects on the surface or inside the glass.

Phase contrast— Great attention is also being paid to phase contrast, a technique which permits the determination of the small irregularities of a wave front by transforming the phase differences corresponding to these distortions into amplitude (or intensity) variations. The sensitivity can be increased so that optical path differences of a small fraction of a wavelength can be detected. Phase contrast is now widely used by microscopists to detect small variations of refractive index, for example in the nuclei of cells, but up to now special 'phase contract objectives' had to be used. Two attempts have been made in the Institute to develop methods of transforming any microscope into a phase contrast microscope. The results are very good and it is hoped that expensive construction of special phase contrast objectives can now be avoided.

PERCEPTION OF IMAGES

Optical images are generally perceived by the eye; sometimes they form an impression on a photographic plate, or they are formed on a photocell or other receptor. The properties of the eye, or of the photographic plate, have to be taken into account if we desire to know the resolving power obtained.

For the eye a long series of experiments were made before the 1939–45 war by A ARNULF to determine the specific resolving power of the eye in various conditions, using an object formed periodically by equidistant parallel white lines on a black background, i.e. the same test as that used by Foucault. The results were analysed and it was stated that the conditions of observation could be defined by three factors: *a* the brightness of the object, *b* the contrast (the background itself being not perfectly dark) and *c* the diameter of the pupil of the eye. Terms of those parameter curves giving the resolving power of the eye have been published[6].

In interpreting the results it seemed that a minimum value for the contrast of the retinal image was necessary to separate periodic structure of the image. Further researches have been performed on the same subject and the perception of a single line or of the limit of two surfaces of slightly different brightness are being studied to elucidate the way in which the retina perceives the images for various conditions of illumination. The speed of variation of the illumination in the image seems to be an important factor but its role has yet to be made clear.

A parallel study of photographic plates is being made, it seems that there are great similarities with the behaviour of the eye, but the influence of diffusion in the emulsion is not yet fully understood. A series of experiments is being performed on that subject by M MARQUET.

STUDY OF GLASS

Great attention is being paid to methods of testing the quality of glass; the most dangerous defect seems to be lack of homogeneity. A new interferometric apparatus is being developed for rapid testing of pieces of glass. A systematic study of the physico-chemical properties of glass is also being made by N Winter. When temperature is varied, interesting changes occur in various physical properties and new transformations of the structure are to be expected. A knowledge of these transformations is very important in determining the proper thermal treatment to be applied to various glasses to secure perfect freedom from internal tensions and birefringence. Moreover, important contributions may be made to the problem of the structure of glass.

GLASS GRINDING AND POLISHING

High quality polishing is desirable in special instruments such as Lyot's coronograph[6] which has been designed to study the solar corona by blotting out the image of the sun itself. The great difficulty is that the brightness of the sun is about one million times that of the corona, and in such conditions diffusion by the optical surfaces has to be very small to prevent error due to stray light from the mass of the sun. Very low diffusion involves high quality polishing. The quality of polishing can be tested by phase contrast: small irregularities of glass surface appear as variations of illumination in the image of the objective and at the same time lack of homogeneity is detected. By taking two photographs at different orientations it is possible to locate the defects. A stereoscopic view of a coronograph objective can be such that small variations in optical path amounting to a few Angströms are detected.

Grinding and polishing of parabolic surfaces can now be carried out rapidly by a procedure based on the single properties of paraboloids due to F Dourneau and J Demarcq[7]. The surfaces obtained are sufficiently accurate for use in eyepieces, where they are very useful for correcting astigmatism. They can also be used in current objectives wherever precision greater than a few wavelengths is not required.

SURFACE COATING

'Blooming' of lenses is now very commonly used: a thin layer of magnesium fluorite or any material having a low refractive index is evaporated on to the glass surface. When the layer has the correct thickness ($\lambda/4$) interference between the two vibrations reflected on the two surfaces of the layer gives a very low resultant reflection. Thus it is possible to prevent losses of light by reflection, and what is more important, to cut down stray light.

Various processes of surface coating have been studied in the Institute of Optics and a general theory of the propagation of light waves in multiple layers, based on matrix algebra, has been elaborated by F Abelès[8]. A method for measuring the refractive index of materials in thin layers has been derived. Many applications can be found, for example the remarkable improvement of the reflecting power of metals when they are coated with a conveniently thin layer. The technique for forming thin layers is also being studied in the laboratory; the relation between the adhesion of the layers on the glass and the method of cleaning the surfaces by discharge or heating (according to the characteristics of the apparatus), establishment of layers of silicon monoxide (protecting layers) or iron oxide (half transmitting layers) *etc*.

PHOTOMETRY

The techniques of photometry have been improved by the construction of new apparatus which secure freedom from various errors. Two types of monochromators have been constructed by F Desvignes. A double monochromator with high precision reflecting optics is used for testing work which gives a very pure radiation and makes change of wavelength very easy. There is also a simple monochromator based on a new idea which gives a very low proportion of stray light, intermediate between that of simple and double monochromators. A photoelectric amplifier has been developed by J Terrien and F Desvignes[9]. It is used for high precision work.

Visual photometry has also been improved by a special study of the effect of diffraction by the separation line in photometric cubes. A complete visual photometric equipment in monochromatic light has been designed. Colorometry is also studied: new apparatus invented by F Blottiau[10] is being tested and will soon be ready for rapid and high precision colorimetric comparisons.

WORK ON TESTING METHODS

A great part of the activity of the Institute of Optics comprises work to improve testing methods. This subject can be divided into three main parts:

a high precision measurements related to technical optics *e g* a great number of index measurements, goniometric studies of prisms, length and curvature measurements.

b quality testing of various optical systems. Special problems concerned with correction of aberrations, resolving power *etc* are referred to the Institute.

c photometric, spectrophotometric and colorimetric measurements. Sources of light, absorbing glasses, papers, paints and various media are studied for photometric properties.

The Institute of Optics is, in fact, the central testing laboratory for optics in France.

PUBLICATIONS AND MEETINGS

The activities of the Institute of Optics are extended to publishing the *Revue d'Optique* and various other periodicals and books dealing with astrophysics, geophysics and photography Original papers are published in full in a special publication, *Communications des Laboratoires de l'Institut d'Optique*

The Institute also plays an important part in international meetings In 1946 a meeting was held in Paris between European scientists and their English or American colleagues to re-establish many contacts Other meetings in 1948 were the *Commission Internationale d'Optique* held in Holland and a conference on thin layers held in Marseille

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Miscellaneous Notes

ROYAL SOCIETY

At its meeting on 16 March the Royal Society elected the following into the Fellowship

Dr B P Babkin, Physiologist, McGill University, Montreal, Canada, Dr L F Bates, Professor of Physics, University of Nottingham, Dr I A Bennet-Clark, Professor of Botany, King's College, London, Dr B Bleaney, Demonstrator and Lecturer in Physics, Oxford University, Dr L J Comrie, Director, Scientific Computing Service Ltd, London, Dr C A Coulson, Professor of Theoretical Physics, King's College, London, Dr L R Cox, Assistant Keeper, Department of Geology, British Museum (Natural History), Dr H S M Coxeter, Professor of Mathematics, University of Toronto, G H Cunningham, Director, Plant Diseases Division, Department of Scientific and Industrial Research, Auckland, New Zealand, Dr W J Elford, Biophysicist, National Institute of Medical Research, London, S B Gates, Senior Principal Scientific Officer, Ministry of Supply (Air), Dr C A Hoare, Protozoologist to the Wellcome Laboratories of Tropical Medicine, London, Dr L Howarth, Professor of Applied Mathematics, University of Bristol, Dr E R H Jones, Professor of Organic Chemistry, University of Manchester, Dr A J P Martin, Biochemist, National Institute for Medical Research, London, Dr D F Martyn, Principal Scientific Officer, Commonwealth Scientific and Industrial Research Organization, Solar Observatory, Canberra, Australia, Dr R A Morton, Professor of Biochemistry, University of Liverpool, Dr R J Pumphrey, Professor of Zoology, University of Liverpool, Dr A G Shenstone, Professor of Physics, Princeton University, U S A, formerly Scientific Liaison Officer in London of the Canadian National Research Council, Dr H E Shortt, Head of the Department of Parasitology, London School of Hygiene and Tropical Medicine, Dr M Stacey, Professor of Chemistry, University of Birmingham, Dr L E Sutton, Demonstrator and Lecturer in Physical Chemistry, Oxford University, R L M Synge, Biochemist, Rowett Research Institute, Aberdeenshire, Dr B P Uvarov, Director, Anti-Locust Research Centre, British Museum (Natural History), Dr F C Williams, Professor of Electro-Technics, University of Manchester

UNIVERSITY APPOINTMENTS

Australian National University, Canberra— Dr E W Titterton will be Professor of Physics and will work with Professor M Oliphant, F R S, in the Research School of Physical Science

London— Dr J E Smith has been appointed to the University Chair of Zoology, tenable at Queen Mary College, from 1 October 1950

The title of Professor of Agricultural Chemistry in the University has been conferred on Dr R L Wain in respect of the post held by him at Wye College

The title of Reader in Bacteriology in the University has been conferred on Dr S E Jacobs in respect of the post held by him at the Imperial College of Science and Technology

The following have had the title of Professor Emeritus in their various subjects conferred on them

Dr E N da C Andrade, f r s, Quain Professor of Physics at University College from 1928 to 1949

C S Gibson, o b e, f r s, who has held the Chair of Chemistry at Guy's Hospital since 1921

Dr H Hartridge, f r s, who held the Chair of Physiology at St Bartholomew's Hospital Medical College from 1927 to 1947

Sir Ian Heilbron, d s o, f r s, who held the Chair of Organic Chemistry at the Imperial College of Science and Technology from 1938 to 1949

Makerere University College, East Africa— Professor B de Bunsen, Acting Principal, has been appointed Principal

Manchester— Dr J L Matheson, m b e, has accepted appointment as Beyer Professor of Engineering and Director of the Whitworth Laboratories

L'ACADÉMIE DES SCIENCES

Professor E N da C Andrade has been elected Correspondent for the Section of General Physics

AWARD

C C Pounder has been awarded the James Clayton Prize by the Institution of Mechanical Engineers in recognition of his work for progressive design for steam turbines and diesel engines

BUILDING RESEARCH STATION

Preliminary experiments on the foaming of clays to make lightweight insulating materials have been made So far the results with brick clays have been unsatisfactory Small specimens with a reasonably fine porous structure were made with ball clay Work on concrete aggregates has included investigations of the possibilities of using Cornish china clay as an aggregate, of limestone aggregates, and of methods of test for silt content Lightweight aggregates such as clinker, vermiculite, expanded clay and foamed slag have also been studied The programme of investigations on steam curing of concrete has been continued and its scope widened Pilot scale test plant has been installed As a first step in research on quality control of concrete a study has been made of the degree of quality control exercised in factories and by firms of building and civil engineering contractors

Alternatives to limewash, containing tallow, as a white surface treatment for bituminous roofing materials have been tested Tallow is scarce and wool grease may be used although it is not quite so durable Trials of paints economizing in linseed oil have been continued A number of types of flooring material for use as alternatives for timber have been studied and several new varieties of building board have also been tested for such properties as weight and density, spread of flame, resistance to impact, ease of decoration *etc*

New Books

Electronic Theory of Organic Chemistry

M J S DEWAR

(*xi+324 pp, illus, 9½ in by 6 in*)

London Oxford University Press 1949 30s net

With the advance of the electronic theory of valency through the applications of quantum mechanics it was inevitable that its consequences should spread into the field of organic chemistry Here a large body of unified knowledge and many general principles and reaction types are available both to test the results of the theory, and also to provide problems the solution of which in terms of the electronic theory would suggest new advances in the novel interpretation of reaction mechanisms not fully explained by the classical theory The main outlines of the newer electronic theory are now sufficiently clear and precise to make the subject one which it is desirable to study in conjunction with the more familiar aspects of organic chemistry, and a book suited to the needs of students is desirable It may be said at the outset that Dr Dewar has succeeded in writing a very clear and interesting account of the field, and his own contributions to it are a guarantee that he has both the knowledge of his subject and the ability to convey this knowledge to others which are essential to the production of a satisfactory book The mathematical aspects of the wave equation which underly its applicability in this field are not particularly difficult or advanced, since they ultimately involve only algebraic or trigonometrical functions, but the technique is unfamiliar to organic chemists A more serious difficulty is that the limit of rigorous mathematical treatment is reached long before anything nearly so complicated as the systems of interest to chemists is reached, and the procedure is actually a different one, certain semi-quantitative results being turned to good use in a rather rough and ready way which conceals its weakness from the uninitiated. In the very clear and interesting chapter iv on the replacement reaction, for example, no hint is given of the coarse approximations which were made in the quantitative ground work, and of the resulting insecurity of the results. The author has some hard things to say of others, and there is quite often a cocksureness in his statements which arouses suspicion; he cannot, therefore, take amiss any remarks about his treatment which suggest themselves to a reader not specially interested in a particular aspect of the theory. One criticism which may be offered is that really important things are often passed over too briefly. It is not made clear, for example, whether what is called resonance energy is an excess of energy in the particular state, or a defect. Sometimes thermochemical equations are used in which energy loss is positive, and in other equations the opposite convention is used. The treatment of the peroxide effect leaves the reader uncertain whether it is real in some cases and not in others. The whole treatment is based on a symbolism making use of dotted lines and deltas, but the exact meaning of this is nowhere explained; it comes into use quite suddenly and without a word of elucidation. It may be quite standard and elementary, but the reviewer failed to understand its interpretation in the sense that he would expect of a symbol in physical chemistry. The author is in too great a hurry to get on to special topics to trouble about such elementary matters.

Complaints are made in parts of the book that some things have been 'almost wilfully misunderstood', but this is only to be expected if they are slurred over in such a perfunctory way. Physical chemists are accustomed to have clear definitions of symbols, and if these are lacking they usually go on to more comprehensible matters. They are not to be blamed for this.

Another weakness of the book is the very loose way in which concepts are used. It is almost inconceivable that organic chemists have confused resonance with tautomerism, yet we are assured that they have done so. The author does not help matters by suggesting that bonding orbitals consist of electron gas, which can lose energy by adiabatic expansion, or by speaking of the 'entropy of a molecule'. The distinctions between mesomerism and resonance, and between bond energy and bonding energy, although they are said to be important, are not clearly explained; it is not suggested that they are not explained at all, but the sentence means just what it says.

There is throughout too pronounced a tendency to dogmatism; when it is said, for example, that the formation of persulphate 'undoubtedly' proceeds through the SO_4^- radical, it may be added that it very probably does not. The tables of bond energies have been compiled in an arbitrary way which is hard to follow and it seems, in fact, as if this matter will finally have to be settled by experiment, formidably difficult perhaps, but the only way after so much theorizing has led to irreconcilable results which no one can say are right or wrong. Minor points of nomenclature, such as the use of 'quadrivalent' in company with 'trivalent' in some instances and 'tervalent' in others, are not trivial in a book intended for students. Usage here was systematized long ago, and divergence is rather an affectation.

The applications of the theory, whatever it may be (and it is not very clear what it is), to groups of topics are interesting and good, particularly when good summaries have been available. The accounts are often much better than those of the original authors. The topics include polar reactions of aliphatic and aromatic compounds, strengths of acids and bases, molecular rearrangements, free radicals and reactions involving them, polymerization, and colour and constitution, that is to say, the well tried and familiar topics which have interested certain chemists and hence must interest certain students.

The treatment of acids and bases is rather old fashioned, the so-called Brönsted theory (here credited to BRONSTED, the unshared pair having been unnecessarily donated to KOLBE more than once) is the foundation, so that important aspects (such as the treatment of the generalized Claisen reaction) of the new theory (just hinted only at the end of the book) are missed. The new work on the Hofmann and Saytzeff rules came too late for inclusion. The treatment of naphthalene is inadequate.

In spite of its faults, the book is so good that it is certain to be very popular with students, and is likely to sell out quickly. It is to be hoped that the author will not follow the example set by some other Oxford books of allowing it to be reprinted several times without revision, after it has become quite out of date. If students do not gain from it any particularly deep knowledge of the electronic theory of organic reactions, they can at least gather from it a stock of *Ephesia grammata* which will serve just as well. The style of the book is clear and attractive, although the reviewer failed to ascertain the precise distinction between reactions which are 'interesting' and those which are merely 'amusing'. The book has its stock of both.

J. R. PARTINGTON

Colorimetric Methods of Analysis

Third edition F D and C T SNELL

Vol I Theory, Instruments, *p*H

(*xii+239 pp, 109 illus, 9 in by 6 in*)

New York D Van Nostrand Co Inc, 1948 $4 50
London Macmillan and Co Ltd, 1948 33*s* 6*d* net

THE new edition of this work, issued in 1936 as two volumes, has now been expanded to three volumes, and it is the first of these which is under review The subject matter includes a brief treatment of the theory underlying colorimetric analysis, a detailed survey of commercial instruments (most of which, with the exceptions of the Lovibond tintometer and comparator and certain Hilger instruments, are only available in the U S A), valuable chapters on accuracy and calculations, and a good account of *p*H measurements by colorimetric methods

The numerous photographs of apparatus are not always satisfactory, the half-tones are frequently fuzzy More line diagrams could be introduced with advantage and these would assist the reader considerably in appreciating the differences between the various commercial instruments The reviewer feels that the advantages (cost, simplicity *etc*) of the simple Nessler tubes—so widely used even at the present time—have not been sufficiently emphasized it does not always follow that a highly expensive colorimeter of necessity gives results of so much higher accuracy as to justify its purchase Numerous references to the literature are given in the text, but these do not appear always to have been selected with due regard to the most recent views and trends Thus a more extended treatment of *p*H scales, with appropriate literature references, might have been included The correction of the proofs has been well done, a page number has been omitted on p 6

The volume provides a sound theoretical treatment of colorimetric analysis, and a detailed but uncritical description of apparatus (largely commercial) employed in the various branches of the subject

A I VOGEL

A Scheme of Qualitative Organic Analysis

F J SMITH and E JONES

(*viii + 320 pp, illus, 8½ in by 5½ in*)

London Blackie and Son Ltd, 1948 17*s* 6*d* net

QUALITATIVE organic analysis is an integral part of advanced organic chemistry courses and it is essential that good textbooks on this topic should be available This book fulfils such a need No claim to originality is made for its subject matter and its value depends upon the method of presentation of this matter The authors have aimed at developing a systematic scheme of examination whereby classes of compounds are eliminated one by one, and in this they have succeeded

The first section of the book deals with the preparation of derivatives and melting and boiling point determinations The second is concerned with detection of elements including fluorine, thus reflecting the growth recently of the organic chemistry of fluorine The third section deals with identification of single substances and is divided into chapters, each dealing with a group of compounds which contain the same elements Each chapter gives details of preliminary and classification tests and of the derivatives which may be prepared The final section of the book deals with separation of mixtures Since the book is intended for students preparing for degree and other examinations it is surprising that the assumption is made that mixtures which contain two compounds of the same group will not be met

With regard to details, the suggestion that it is of little value to prepare derivatives direct from esters is not always valid It is often easier to prepare derivatives of the acid direct from the ester, such as the anilide by the Grignard method, than to prepare them after saponification and isolation of the acid The statement that either maltose or lactose is present if no reduction of Barfoed's solution occurs is misleading as other disaccharides are non-reducing to this solution The inclusion of methods for halogen estimation is useful since the value of quantitative estimations cannot be over emphasized

In view of the wide scope of the book elementary students will probably require guidance in its use It is, however, one which can be thoroughly recommended It contains excellent tables, is well indexed and reasonably priced

T G HALSALL

The Atomic Age

Sir Halley Stewart Lectures for 1948

M L OLIPHANT, P M S BLACKETT, R F HARROD,
B RUSSELL, L CURTIS and D W BROGAN

(*149 pp, 7½ in by 5 in*)

London G Allen and Unwin Ltd 1949 7*s* 6*d* net

THIS is a series of important lucid lectures representing a variety of thoughts on the atomic problem The opinions range from the belief that atomic bombs 'will destroy civilization and may even end by destroying all human life on earth' (Professor CURTIS) to the statement that the contraceptive is 'an invention far more deadly in its potentialities' (Professor HARROD)

It is supposed that a better understanding of the scientific background of atomic knowledge will aid in solving the problems created by the bomb Unfortunately, past experience has shown that popularization of science is almost impossible, in spite of outstanding efforts like the unusually clear lecture presented by Professor Oliphant About thirty years ago there was a tremendous popular demand for information about Einstein's Theory of Relativity All that remained in the non-scientist's mind is the conviction that Einstein is a mathematician and that barely a dozen people are capable of understanding him

Professor Blackett again defends his thesis that the atomic bomb is not a decisive weapon He quotes earlier opinions that war was believed made impossible when firearms and when airplanes were first introduced His arguments on this point seem sound, but the point itself is not well chosen Whether atomic bombs can lead to a military victory or not, their destructiveness is so different from conventional weapons that they will completely alter the character of future wars Professor Blackett warns against a 'preventive war' and advocates that a strictly defensive policy of the West and an attempt to negotiate an agreement with Russia can stop the advance of Communism Unfortunately, he does not say how such negotiations can be made to succeed

Lord Russell's lecture on 'Values in the Atomic Age' is so persuasive that his conclusions sound most alarming We are faced with either extinction of the human race or reversions to barbarism unless the world submits to a single government with a monopoly of armed force He shares with Professor Brogan the view that the United States, playing the leading role, can for the present bring about such a unified armed force But Professor Brogan fears that the hesitancy and uncertain character of American foreign policy may lessen its influence in the world in spite of its beneficial intentions

Professor Harrod, discussing the 'Economic Consequences of Atomic Energy', is very sceptical about its eventual economic advantages and accuses scientists of stressing these benefits because of their guilty conscience after Hiroshima He wishes to stop not merely the manufacture of bombs but also all experimentation on the development of atomic power

In this extreme diversity of thoughts the authors seem, however, more or less in agreement about one important issue, namely the absolute necessity of peace through some sort of world government, perhaps initially in the form of a *Pax Americana*

S A Goudsmit

Practical Section Cutting and Staining

E G CLAYDEN

(viii + 190 pp, 21 illus, 8 in by 5½ in)

London J and A Churchill Ltd, 1948 9s

This small volume, intended primarily as a laboratory handbook for histology technicians, deals thoroughly with the preparation of paraffin wax, frozen and celloidin sections from various tissues, and includes much helpful information gathered from the author's practical experience The common staining reactions, with few exceptions, are described clearly and in adequate detail, but with no discussion of the underlying reasons for the use of the various reagents To quote but two examples, any book of this type would undoubtedly profit greatly by the explanation of the use of such reagents as lithium carbonate (in Bennhold's congo-red staining method for amyloid) or of potassium permanganate followed by oxalic acid (in the osmic acid method for the staining of fat in tissues) Despite such omissions, the detailed instructions given for the various stages in the preparation of the more common paraffin wax sections, namely fixation, dehydration, clearing, embedding and blocking out of the tissue, the use of the microtome, and the staining and mounting of the sections, should prove of value to technicians and others with little practical experience in this field

The book is rendered less attractive by poor English and sentence construction, and unfortunately the standard exhibited by the photomicrographs is not maintained in the line illustrations

M Webb

Books to Come

Metallographie des Magnesiums und seiner technischen Legierungen, *Second edition* W BULIAN and E FAHRENHORST *(viii 139 pp, 250 illus)* Berlin Springer-Verlag *DM 16 50*

Petrology of the Igneous Rocks, *Tenth edition* The late F H. HATCH, A K and M K WELLS *(469 pp, 151 illus, demy 8vo)* London George Allen and Unwin Ltd *25s net*

Modern Interferometers C CANDLER *(c 500 pp, illus, royal 8vo)* London Hilger and Watts Ltd Hilger Division *c 50s*

Roads Their Alignment, Lay-out and Construction R G BATSON *(224 pp, illus, royal 8vo)* London Longmans, Green and Co Ltd *21s net*

Die Erzmineralien und ihre Verwachsungen P RAMDOHR *(c 900 pp)* Leipzig Akademie-Verlag *DM 70 00*

Elektronenoptik, I Grundlagen der theoretischen Elektronenoptik A RUSTERHOLZ *(256 pp, 118 illus)* Basel Verlag Birkhauser. *S Fr 29 00*

RESEARCH SUPPLEMENT

Azobenzene Part I Vapour Pressure of Cis- and Trans-azobenzene

N F H BRIGHT, B Sc, Ph D, A R I C, T CARSON and G A DYSON

The vapour pressure of pure cis and trans isomers of azobenzene have been measured by an effusion technique over the temperature range 30 to 62°C The results for the two isomers can be represented by the equations $\log_{10} p = -(3{,}911/T) + 9\,721$ *for the trans isomer and* $\log_{10} p = -(3{,}914/T) + 9\,652$ *for the cis isomer, where* p *is in mm of mercury and* T *is the absolute temperature Both isomers can be vaporized within this temperature range and recondensed without observable interconversion*

In view of the application of azobenzene in the field of pesticide dispersion by the smoke technique[1-3], it was considered of interest to determine its vapour pressure over a convenient range of temperature The subject is also of more fundamental interest in that doubt has been expressed recently concerning the separate existence of the two geometrical isomers of azobenzene[4]

The practical aspect of the problem was to provide data for assessing the toxicity of the vapour and the risks involved in handling the solid, and also to give some guide as to the persistence of the material when laid down as a pesticidal deposit from smoke The product commonly available for commercial purposes contains approximately 98 per cent of the *trans* isomer Hence it was decided to study the vapour pressure of the pure *trans* isomer, to provide data to answer the practical problem, and also to include measurements on the pure *cis* isomer owing to their fundamental interest

EXPERIMENTAL

The isomers were prepared from commercial azobenzene according to a method which combines that of **Hartley**[5] with that given by **Cook**[6], details are as follows .

> *Trans*-azobenzene was prepared by fractional precipitation with water from an acetone solution of commercial azobenzene, m pt 68°C *Analysis* found (by microanalysis) C 79 0%, H 5 6%, N 15 5% Calculated for $C_{12}H_{10}N_2$, C 79 1%, H 5 5%, N 15 4%
>
> *Cis*-azobenzene A saturated solution (about 10% by weight) of commercial azobenzene in 500 ml acetic acid containing 10 ml water was exposed to sunlight for 4 hr in a flat enamelled dish covered with a sheet of plate glass The *trans*-azobenzene was then precipitated by adding 450 ml of water and filtered off A further 500 ml of water was added to the filtrate which was then extracted with 300 ml of chloroform The extract was washed with water, dried over anhydrous sodium sulphate, and the chloroform evaporated off under vacuum The crude crystalline product so obtained was dissolved in light petroleum and subjected to chromatographic separation through a column of alumina The *cis*-azobenzene was strongly adsorbed near the top of the column while the *trans*-azobenzene was only weakly adsorbed and was readily washed through with petroleum The *cis*-azobenzene was eluted with light petroleum containing 1% of methanol , the extract was washed with water and dried over anhydrous sodium sulphate The petroleum was evaporated off under vacuum and the product recrystallised from light petroleum between + 15°C and − 15°C M pt 70–71°C *Analysis* found (by microanalysis) C 79 0%, H 5 6%, N 15 6% Calculated for $C_{12}H_{10}N_2$, C 79 1%, H 5 5%, N 15 4%

The method of determining the vapour pressures was that involving the effusion technique originally employed by **Knudsen**[7] and later developed by **Egerton**[8] for metals

The sample was heated for a known time at a constant measured temperature in a small copper vessel, 1 cm diam by 2 5 cm long, with a tightly fitting lid The vessel had a small cylindrical orifice of known dimensions through which the azobenzene vapour could effuse as a molecular beam into a space evacuated to 10^{-6} mm mercury by an efficient high vacuum pumping system It is necessary, in order that the method should be valid, for the mean free path of the effusing molecules at, for instance, the vapour pressure of the material under investigation, to be long in comparison with the dimensions of the orifice It can be shown that this condition is not obeyed if the pressure to be measured is markedly in excess of 10^{-2} mm mercury

The vapour pressure p of the material, expressed in mm mercury, is given by the formula

$$p = \frac{g}{5\,83 \times 10^{-2}\, Wat\sqrt{(M/T)}} \qquad (1)$$

where g is the weight in gm of material effused through the orifice, estimated by the loss in weight of the container, and azobenzene, a is the cross sectional area of circular orifice, sq cm, t the time of duration of experiment, sec, and T the mean absolute temperature of experiment, measured by means of a copper/constantan thermocouple affixed to the bottom of the copper vessel. M is the molecular weight of the material under investigation, and W is the probability of effusion through the orifice without returning to the inside of the vessel, for a given molecule. Values of W for orifices of various length/cross sectional area ratio have been calculated by CLAUSING[9]

The experimental values obtained are quoted in *Table I*

Table I Experimental Results

Trans azobenzene		*Cis azobenzene*	
Temperature of experiment °C	*Vapour pressure of material* mm mercury × 10³	*Temperature of experiment* C	*Vapour pressure of material* mm mercury × 10³
62.0	12.4	59.1	8.82
59.1	8.40	58.0	5.91
48.9	3.56	48.9	3.03
48.5	3.44	48.9	2.93
40.1	1.73	40.5	1.56
39.8	1.91	40.2	1.38
33.1	1.08	31.9	0.871
31.0	0.386	31.0	0.329
		31.0	0.339

These experimental results gave the following vapour pressure equations connecting $\log_{10} p$ and $1/T$ when fitted by the method of least squares

$$Trans \text{ isomer} \quad \log_{10} p = -\frac{3{,}911}{T} + 9.721 \qquad (2)$$

$$Cis \text{ isomer} \quad \log_{10} p = -\frac{3{,}914}{T} + 9.652 \qquad (3)$$

where p is the vapour pressure in mm mercury, and T is the absolute temperature of determinations

DISCUSSION

The above equations correspond to the following latent heats of vaporization, assumed constant over the temperature ranges investigated

trans isomer	98.2 cal/gm
cis isomer	98.3 ,,

This shows that the two isomers have substantially the same latent heat of vaporization.

Further statistical analysis of the two sets of vapour pressure figures shows that, although the two lines obtained from the equations are almost exactly parallel, the difference between the intercepts for the two isomers is just significant and that it is probably slightly better statistically to represent the points as two discrete sets lying about two parallel lines rather than to regard them as one set lying all about one straight line

It is of great importance to note that the material evaporated in these vapour pressure determinations, when recondensed to the solid phase on a cooled target, was shown by infra-red analysis to be the same as the original material. That is *trans* recondensed as *trans* but *cis* showed no detectable *trans* in the condensate and appeared identical with the starting material. This indicates that both isomers have, at least, a reasonable stability in the vapour phase, and that a finite time is required, even as vapour, for the *cis* isomer to be converted into the *trans* in the temperature range 30 to 62°C

Some further results obtained on azobenzene made by recrystallizing the commercial material from ether without any precautions to exclude actinic light, and thus presumably containing a mixture of *cis* and *trans* isomers, gave vapour pressure figures approximately equal to the sum of the vapour pressures of the two separate isomers, as would be expected for a mixture of two discrete and non-interacting compounds

The fact that the two compounds show additive vapour pressures, their stoichiometrical identity as shown by microanalysis and their different infra-red spectra[10] all support the reality of the existence of the two materials as *cis* and *trans* isomers of azobenzene and all conflict with the views of HODGSON[4] who considers the *cis* isomer to be a double compound of hydrazo- and azoxybenzene

The authors' thanks are due to J C Cuthill for the preparation of the pure isomers

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Azobenzene Part II: Infra-Red Spectra of Slurries of Cis- and Trans-azobenzene

K S TETLOW, B A

Infra-red spectra have been recorded of slurries of cis- and trans-azobenzene and hydrazobenzene Key bands of the cis and trans isomers have been noted, enabling characterization of samples The interconversion of the isomers can be followed by measurements on these bands Christiansen transmission peaks were observed in the slurries and were taken into account when interpreting the spectra

IN order to characterize samples of azobenzene used in pesticidal smoke formulations, infra-red absorption spectra have been recorded of *cis*- and *trans*-azobenzene , the work is reported in view of the current interest in the geometrical isomers of azobenzene[1] These compounds provide a good example of how an infra-red spectrogram can be used to fingerprint, and provide an estimate of the composition of an organic substance

EXPERIMENTAL

The samples of azobenzene were identical with those used for measurements of vapour pressures[2] Because of the reported facile *cis* → *trans* change of azobenzenes in solution, especially under the influence of ultra-violet light, spectrograms were obtained of slurries of the materials ground to a paste with liquid paraffin

The material was first ground dry in an agate mortar and was then wetted with liquid paraffin and further ground to a smooth paste, the operations being carried out in a dimly lit room in instances where possible isomerization might occur if grinding were conducted in daylight The slurry was spread between rock salt plates in the desired thickness and placed at an external focus of one beam in a modified Hilger *D209* infra-red spectrometer, operating as a single beam camera recording instrument

Energy traces were obtained for the region 2-15μ, from which percentage absorption plots could be made by the recording of the ' background ' energy Little useful measurement could be made in the region of strong aliphatic C—H vibrations (2,900, 1,460 and 1,375 cm^{-1}) owing to absorption by liquid paraffin Also, owing to broadness of bands in the solid and uncertainty of background position because of irregular scattering, it was not felt that an accurate representation of the percentage absorption in the 5-8μ region of water vapour absorption was possible In consequence attention was focused on the 8-15μ region and band positions noted wherever possible in the 2-8μ region Correlations between absorption band frequency and vibrations of atomic groupings[3] are far less well defined in the former region except in certain cases such as the ν_4 (a_{2u}) mode of benzene and associated vibrations in substituted benzene, where the hydrogen atoms move through the plane of the carbon ring Thus any assignments made can be only tentative at this stage

In all the specimens studied strong anomalous dispersion effects were noticed at certain bands due to the infra-red Christiansen filter effect[4] In drawing percentage absorption curves, *Figure 1*, from the recorded spectrograms, Christiansen transmission peaks and the associated small minima on the high frequency side of the absorption band concerned were smoothed out to present a curve that more nearly represents the absorption contour of the substance

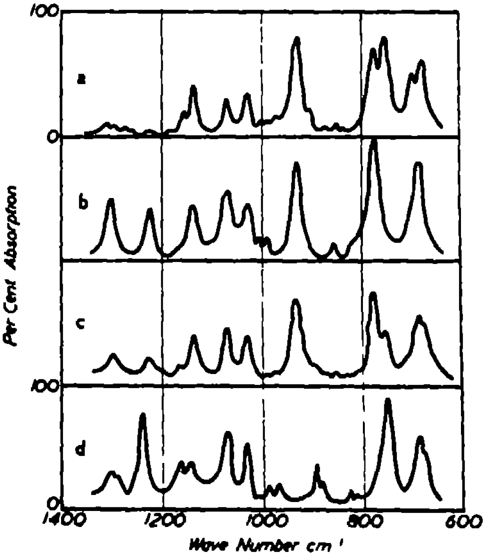

Figure 1 *Infra-red absorption curves* a *cis-azobenzene* b *trans-azobenzene* c *cis-azobenzene exposed to sunlight for two hr* d *hydrazobenzene*

- *c* IPPC, 0 25 per cent in inert filler applied at 2 68 gm/kg of tubers
- *d* IPPC, 0 5 per cent in inert filler applied at 2 68 gm/kg of tubers
- *e* IPPC, 1 per cent in inert filler applied at 2 68 gm/kg of tubers

Thirteen trials scattered over England and Northern Ireland were completed with the results shown in *Table III*

The results show clearly that IPPC was much superior to MANA in reducing sprouting of tubers and a 1 per cent IPPC dust under field conditions gave excellent results A correlation between date of examination and degree of sprouting exists for the IPPC treated tubers and this suggests that the method, whilst primarily of practical importance for long keeping of ware, is not ruled out for use on seed potatoes Exposure to air may rapidly destroy the sprout inhibiting effect

Extensive toxicity tests are now in progress and results must be awaited before IPPC can be recommended for use The effectiveness of IPPC for the purpose detailed above has also been recently described elsewhere[7]

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Bond Refractions and Bond Parachor of the C=N Link

We have prepared four series of liquid compounds containing the C=N link and have determined the molecular refractivities for the *C*, *D*, *F* and *G'* lines and also the parachors The constants for the C=N link were evaluated with the aid of the values previously reported[1] and our own unpublished figures

Simple aliphatic aldoximes— The constants for the following bonds were used C—H, C—C, N—O and O—H (alcohols) The results are given in *Table I*

Table I Bond Refractivities and Bond Parachor for C=N *from Aldoximes*

Compound	*Bond refractivities*				*Bond parachor*
	C	*D*	*F*	*G'*	
$\mathrm{MeCH{=}NOH}$	3 61	3 62	3 69	3 77	35 8
$\mathrm{EtCH{=}NOH}$	3 56	3 61	3 68	3 77	34 3
$\mathrm{Pr^{a}CH{=}NOH}$	3 61	3 67	3 74	3 83	33 6
Mean	3 59	3 63	3 70	3 79	34 6

Simple aliphatic ketoximes— The bond constants employed in the calculation of those of C=N were similar to those for aldoximes The results are summarized in *Table II* It will be noted that the bond parachor falls as the molecular weight increases

Table II Bond Refractivities and Bond Parachor for C=N *from Ketoximes*

Compound	*Bond refractivities*				*Bond parachor*
	C	*D*	*F*	*G*	
$\mathrm{MeEtC{=}NOH}$	3 50	3 62	3 72	3 79	30 7
$\mathrm{Et_2C{=}NOH}$	[illegible]	3 57	3 64	3 71	28 0
$\mathrm{MePr^{a}C{=}NOH}$	3 58	3 64	3 73	3 70	28 9
$\mathrm{EtPr^{a}C{=}NOH}$	3 45	3 50	3 58	3 64	26 8
$\mathrm{Pr^{a}_2C{=}NOH}$	3 49	3 48	3 58	3 64	23 6
Mean	3 51	3 56	3 65	3 71	?

O-Alkyl ethers of simple aliphatic ketoximes— The constants required were those for C—C, C—H, N—O and C—O (ethers) The results are collected in *Table III*

Table III Bond Refractivities and Bond Parachor for C=N *from Ketoxime-O-alkyl ethers*

Compound	*Bond refractivities*				*Bond parachor*
	C	*D*	*F*	*G*	
$\mathrm{Me_2C{=}NOMe}$	3 64	3 68	3 74	3 86	—
$\mathrm{Me_2C{=}NOEt}$	3 81	3 85	3 93	4 05	32 7
$\mathrm{Me_2C{=}NOPr^{a}}$	3 68	3 73	3 80	3 91	32 1
$\mathrm{MeEtC{=}NOEt}$	3 79	3 78	3 85	3 94	—
$\mathrm{MeEtC{=}NOPr^{a}}$	3 50	3 56	3 65	3 72	—
$\mathrm{Et_2C{=}NOEt}$	3 62	3 67	3 77	3 85	28 1
$\mathrm{Et_2C{=}NOPr^{a}}$	3 56	3 60	3 71	3 79	29 0
$\mathrm{MePr^{a}C{=}NOEt}$	3 76	3 81	3 90	3 99	—
$\mathrm{MePr^{a}C{=}NOPr^{a}}$	3 63	3 67	3 77	3 87	—
$\mathrm{EtPr^{a}C{=}NOEt}$	3 77	3 80	3 92	3 99	29 6
$\mathrm{EtPr^{a}C{=}NOPr^{a}}$	3 70	3 73	3 87	3 92	28 8
$\mathrm{Pr^{a}_2C{=}NOEt}$	3 77	3 80	3 93	3 98	27 1
$\mathrm{Pr^{a}_2C{=}NOPr^{a}}$	3 78	3 81	3 93	4 00	27 1
Mean	3 69	3 73	3 83	3 91	29 3

Simple aliphatic ketazines— The constants required for the computation of C=N were those for C—C, C—H and N—N (from hydrazines) The results are summarized in *Table IV* It will be noted that the refractivities for the C=N link are considerably higher than the values deduced from the first three series this must be attributed to the presence of the conjugated system C=N—N=C

Table IV Bond Refractivities and Bond Parachor from Ketazines

Compound	Bond refractivities C	D	F	G	Bond parachor
$Me_2C{=}N{-}N{=}CMe_2$	4 33	4 38	4 56	4 65	32 5
$MeEtC{=}N{-}N{=}CMeEt$	4 31	4 36	4 56	4 63	31 3
$Et_2C{=}N{-}N{=}CEt_2$	4 23	4 29	4 48	4 56	28 5
$MePr^{a}C{=}N{-}N{=}CMePr^{a}$	4 34	4 38	4 59	4 67	30 0
$EtPr^{a}C{=}N{-}N{=}CEtPr^{a}$	4 28	4 36	4 56	4 69	27 4
$Pr^{a}_2C{=}N{-}N{=}CPr^{a}_2$	4 37	4 44	4 64	4 71	25 4
Mean	4 31	4 37	4 57	4 65	29 2

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Ultraviolet Absorption Spectra of the Two Phenylnaphthalenes

DATA are available in the literature of the ultraviolet absorption spectra of 1-phenylnaphthalene and of 2-phenylnaphthalene Measurements on synthesized and purified samples of these two hydrocarbons confirmed the discrepancies between the data recorded by various authors and for this reason the synthesis of the two phenylnaphthalenes was repeated and their absorption spectra were measured both with isooctane and ethylalcohol as solvents The phenylnaphthalene samples were prepared by Dr SULZBACHER of the Grosvenor Laboratory, London Both samples of 1-phenylnaphthalene, *GL53* and *GL53II*, had been prepared in the same way by the Grignard reaction of 1-bromonaphthalene and *cyclo*hexanone 2-phenylnaphthalene *GL58* resulted from the succinoylation of diphenyl followed by Clemmensen reduction and cyclization 2-phenylnaphthalene *GL60* was obtained by cyclization of phenylglycol by sulphuric acid

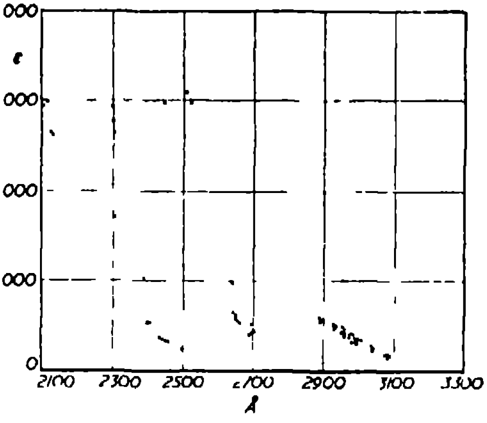

Figure 1 Graph of results • 1-phenylnaphthalene in isooctane × 2-phenylnaphthalene in isooctane

The accompanying diagram, *Figure 1*, represents what we regard as being the most reliable phenylnaphthalene spectra (concerning the purity of the hydrocarbons) at present *Tables I* and *II* summarize the absorption characteristics of 1-phenylnaphthalene

Table I Absorption Characteristics of 1-phenylnaphthalene

	Sample GL53 in isooctane		Sample GL53 II in isooctane		Sample GL53II in ethylalcohol		1-phenylnaphthalene in cyclohexane[1]		1-phenylnaphthalene in 95 per cent ethanol[1]	
	Å	ε	Å	ε	Å	ε	Å	ε	Å	ε
Maximum	2 240	69,900	2 244	71,000	2 248 5	72 500	2,273	61,500	2,290	56,900
Maximum	2 848	10,980	2 857	11,950	2 841 5	11 650	2,877	11,000	{ 2 847 2,880	9,120 9,180

Table II Absorption Characteristics of 2-phenylnaphthalene

	Sample GL58 in isooctane		Sample GL60 in isooctane		Sample GL58 in ethylalcohol		Sample GL60 in ethylalcohol		2-phenylnaphthalene in cyclohexane[1]		2-phenylnaphthalene in 95 per cent ethanol[1]		2-phenylnaphthalene in ethylalcohol[11]		2-phenylnaphthalene in ethylalcohol[6]	
	Å	ε	Å	ε	Å	ε	Å	ε	Å	ε	Å	ε	Å	ε	Å	ε
Maximum	—	—	2 111	61 300	—	—	—	—	2,115	31,600	2 137	40 400	—	—	—	—
Maximum	2,486 5	55,500	2 496 5	69,200	2 498 5	54 750	2,491	66 250	2,499	48,100	2,500	46 900	2 510	58,000	2,495	67,100
Maximum	2,796	19,000	2 851	12,500	2 838	13,150	2 857	12 730	2,845	11,500	2,863	11,900	2,800 2,870	12,700 12,700	2,833	14,900

and of 2-phenylnaphthalene found by various workers

It would appear from these results that there was no appreciable solvent effect with the two phenylnaphthalenes, in contrast with phenanthrene[4] Comparing the results obtained with the two differently prepared samples of 2-phenylnaphthalene we are inclined to think that the material *GL60* was the purer of the two

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Mechanism of Aromatic Halogenation, The Chlorine Cation, Cl+

Considerable discussion has centred on the question of the participation of halogen cations in halogenation reactions, but significant evidence has been meagre[1-6] The application of physical methods having recently demonstrated the formation and effectiveness of the nitronium ion NO_2^+ in nitration reactions[7], it seemed appropriate to investigate the mechanism of halogenation along similar lines The kinetic results provide decisive evidence of the participation of the chlorine cation in chlorination

Using hypochlorous acid as the halogenating agent ([HOCl] ≃ 0 002M at 25°C) in water in the presence of sulphuric or perchloric acids, with special precautions to eliminate the intervention of chlorine, the reaction is of the first order with respect to hypochlorous acid, but for the more reactive aromatic compounds the rate of halogenation is independent of the concentration and nature of the compound substituted Disregarding for the moment a dependence on the acidity of the solution, we have

$$v = k\,[\mathrm{HOCl}] \qquad (1)$$

In the presence of silver sulphate or perchlorate this result has been established *e g* for anisole (initial [anisole] = 0 003–0 01M) Under the same experimental conditions, quinol dimethyl ether (0 004M) and phenol (0 003–0 008M) gave the same rate coefficients as anisole Thus for all these compounds, the first order rate coefficient in the presence of 0 011M sulphuric acid had the uniform value $3\ 1 \times 10^{-4}\,\mathrm{sec}^{-1}$ at 25°C Variation of the concentration of silver ions ([Ag+] = 0 005–0 1M) did not appreciably affect the rate For less reactive structures, a dependence of the rate on the compound substituted is observed, the rate equation becoming

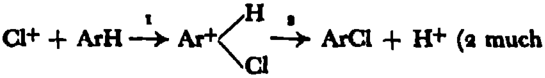
$$v = k\,[\mathrm{HOCl}]\,[\mathrm{ArH}] \qquad (2)$$

The situation is clearly analogous to that in nitration[8] For adequate concentrations of fairly reactive compounds the kinetically fundamental process in halogenation under the conditions described is shown to be localized in the substituting agent This process consists of a rate-determining fission which is facilitated by a preliminary proton uptake

$$\mathrm{Cl}\,|\!-\!\mathrm{X} \rightleftharpoons \mathrm{Cl}^+ + \mathrm{X}\ (\mathrm{X}-\mathrm{OH},\overset{+}{\mathrm{O}}\mathrm{H}_2)$$

Since a measurably slow change in the reagent cannot depend solely on proton transfers, which are rapid in oxyacids, only the heterolysis of the Cl—O bond as shown could constitute a slow (and therefore activated) process providing an electrophilic substituting agent For compounds and conditions which can effect a sufficiently rapid removal of Cl+, the rate of halogenation is independent of the aromatic substance If a change to a less reactive compound, or to an insufficiently high concentration of a given compound, allows the chlorine cation to approach a stationary concentration, the rate of chlorination becomes dependent on the aromatic compound

A kinetic relationship of type 2 has been reported for hypobromous acid[1, 4-6] By itself it is not decisive The observation of first order kinetics of type 1 and the change of kinetic order 1 → 2 has, however, the same importance for halogenation as the similar discoveries for nitration and for alkyl halide hydrolysis had for the mechanism of these processes Just as these kinetic observations established a rate-determining heterolysis to give either the nitronium ion or a carbonium ion, so the present results demonstrate the formation and effectiveness of the chlorine cation in aromatic chlorination under the conditions described As in nitration[8, 10] the transformation of the cationic reagent into an aromatic substituent is considered to be a two stage process, the proton loss having no kinetic significance



$$\mathrm{Cl}^+ + \mathrm{ArH} \xrightarrow{1} \mathrm{Ar}^+\!\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right. \xrightarrow{2} \mathrm{ArCl} + \mathrm{H}^+$$

(2 much faster than 1)

It is not our thesis that halogen cations are universal precursors in halogenation reactions Conditions were chosen which would suppress the incursion of other possible mechanisms *e g* one depending on the intervention of molecular chlorine, the formation of which, from hydrochloric acid and hypochlorous acid, was observed by SOPER and SMITH[11] to be the rate-controlling process in the chlorination of certain phenols

Similar investigations with other halogenating agents are in progress.

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Causes of Dental Caries

IN a series of investigations[1–8] deposition of calcium salts in osseous tissues was found to be brought about by means of minute quantities of the trace elements strontium and vanadium, whereas these deposits are carried away again by means of traces of zinc and thallium or barium and thallium When the normal balance between the processes is disturbed the teeth are subject to dental caries The enamel of the teeth in places where holes afterwards appear becomes clear and transparent because the underlayer of calcium deposit has disappeared The elements fluorine, silicon, and beryllium were found to be without significance for these processes The experiments were performed with young rats and young guinea pigs and limited to ninety days Some elements might have been supplied to the young animals by their mothers, or they might prove to be of significance during a prolonged experimental period In general fluorine seemed to have a certain bearing upon the problems of dental caries

It is known that the fluorine content of teeth enamel is higher than in the inner osseous tissues of teeth, both in man and experimental animals It has also been proved that in districts where there is a certain fluorine content of drinking water *etc* the frequency of dental caries is lower On the other hand, when the fluorine content of drinking water is too high it has an unfortunate influence on teeth enamel Brushing the surface of the teeth with fluorine compounds has also been tried with some success

A further series of experiments was carried out using the methods already described, it was applied to pregnant, newborn and older varieties of the same experimental animals

The results of all these experiments may be summarized as follows

1 the osseous tissues of the inner part of the teeth are continually renewed, the calcium deposits according to the processes mentioned above and the organic constituents according to other processes which will be described in subsequent papers Both processes occur for as long as the substances needed are supplied in sufficient quantities, and for as long as the enamel is intact Fluorine does not seem to be indispensable for these processes

2 the enamel of the teeth needs fluorine for its proper formation Teeth are covered with enamel during growth, before they emerge from the jaws this enamel is only very slightly renewed during the subsequent life of the teeth, fluorine-containing substances being carried towards the surface when the other calcium deposits are carried away from the teeth

3 when the normal processes in the teeth are disturbed, causing too little calcium to be deposited, the underlayer of enamel disappears, making the enamel more subject to outward attacks This explains why a sufficient supply of fluorine (or fluorine brushing) is not always helpful

4 when too little fluorine is supplied during enamelling of the teeth the enamel becomes less resistant, hence sufficient calcium deposits are not always a protection against dental caries

5 the fluorine must be supplied before or during the enamelling of teeth At other periods a fluorine supply is not so useful, too high a supply being plainly harmful because it is deposited along with the calcium deposits and carried towards the enamelled surface

6 silicon and beryllium were not found to be of any significance in these experiments

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Surface Effect Occurring on High Carbon Steels Heated and Cooled in Vacua

Very little attention appears to have been directed to surface changes taking place during the heating and cooling in vacua of polished metallographic specimens

Some work is however at present being carried out in these laboratories upon such changes, with particular reference to carbon steels

It has been observed that hypereutectoid steels, heated into the austenite region and cooled in high vacua, become covered with a grey-black film, which on a steel of 1 15 per cent carbon content extends over approximately 90 per cent of the surface

Figure 1 Previously polished surface of a 1 15 per cent carbon steel after heating to 1,000°C and cooling in a vacuum Magnification × 100, reduction factor ½ on reproduction

The nature of this film has been investigated by electron diffraction (incident beam), x-ray powder photography and friction measurements These investigations prove conclusively that the film consists of graphite *Figure 1* (× 100) shows the general appearance of a previously polished surface of a hypereutectoid steel after heating at 1,000°C for 2 hr and cooling at approximately 10°C/min in a vacuum maintained throughout the experiment at, or better than, 10^{-5} mm Hg The detailed analysis of the steel (per cent) is as follows carbon 1 15, silicon 0 18, manganese 0 33, phosphorus 0 026, sulphur 0 032, nickel 0 13, chromium 0 05, molybdenum, less than 0 03, copper 0 11

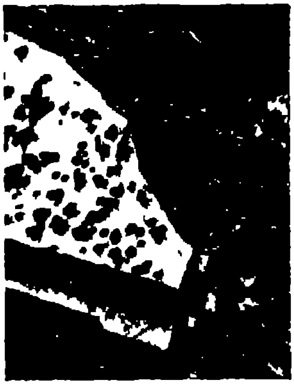

Figure 2 As Figure 1, magnification factor × 500, reduction factor ½ on reproduction

It will be seen that a large part of the surface is covered with a grey-black film of graphite Some parts, however, are still bright and have general shapes resembling austenite grains It will also be seen that these bright regions are occasionally crossed by bands of graphite which are presumably traces of former austenite twins It would thus appear that the film is related crystallographically to the austenite grain structure which the steel possessed at 1,000°C *Figure 2* (× 500) shows the nature of the surface in more detail under slightly obliqued illumination The twin band relationship is again shown and the uneven nature of the graphite film is apparent

Careful control experiments have shown that the graphite formation is not due to deposition from a vapour phase, or to contamination from any external source such as refractory materials It appears to be an inherent and characteristic reaction which can take place on the surface of high carbon content plain carbon steels No traces of graphite can be found in the interior of the steel The extent to which the film formation takes place diminishes as the carbon content is lowered, but it has been observed to a small extent upon steels of eutectoid carbon content (0 83 per cent)

The phenomenon is being investigated further, together with changes taking place when lower carbon content materials are treated similarly, and a more detailed account will be published later

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Outer Brillouin Zones for the Face Centred Cubic, Body Centred Cubic and Close Packed Hexagonal Structures

ALTHOUGH the forms of the first Brillouin zones for a number of metallic structures have been described in several books[1] the forms of the outer zones have received little attention In the course of theoretical investigations on the alloying behaviour of polyvalent metals, and in particular of titanium, it has been necessary to examine the nature of these outer zones and the purpose of this letter is to describe the results of this examination

Face centred structure— The first zone is formed by the planes of type {111} and {200} in *k*-space and has a volume $4/a^3$, where a is the lattice spacing, the zone corresponds to two electrons per atom and overlap from this zone into the next takes place across the {111} faces The next outer zone must be formed by the addition of an extra volume, enclosed by planes of energy discontinuity, on to the {111} faces, and also on to the {200} faces The second zone therefore takes the form of *Figure 1*, which is constructed from the {111} and {200} planes, together with a small contribution from the {311} planes, which cut off the tips of the outermost {111} pyramids This volume lies wholly within the volume enclosed by planes of the type {220}, and also wholly within the volume enclosed by combinations of planes of $(h^2 + k^2 + l^2) > 11$ Neglecting the small volume cut off by the {311} planes, the volume of the zone in *Figure 1* is $8/a^3$, corresponding to four electrons per atom An inscribed sphere of maximum radius would touch the edges of the {111} octahedron (points *a*) at $r = 3/2a\sqrt{2}$ which corresponds with 2 49 electrons per atom With this number of electrons per atom, however, the actual Fermi distribution within the zone would be expected to be far from spherical

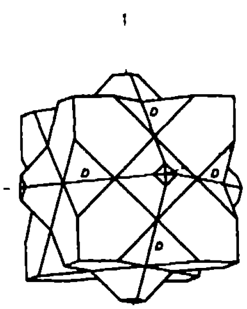

Figure 1 Outer zone for face centred cubic structure

Body centred cubic structures— Here the first zone is bounded by {110} planes in *k*-space and has the volume $2/a^3$ corresponding to two electrons per atom Extra volumes cannot in this case be erected on the {110} faces by extensions of the planes already present, and the next outer zone must be bounded by a new set of planes The set of planes next nearest to the origin of *k*-space is the {200} set, which forms a cube, of volume $8/a^3$, which totally encloses the first zone This cube is, however, intersected by the {211} planes, so that the second zone, bounded everywhere by planes of energy discontinuity, has the form of *Figure 2* Its volume is $7/a^3$ (corresponding to seven electrons per atom), and the maximum inscribed sphere touches the {200} faces at a radius of $1/a$ (corresponding to 4 189 electrons per atom) This zone lies wholly within the volume formed by the next set of planes, of the {220} type

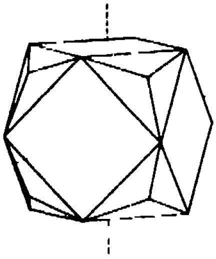

Figure 2 Outer zone for body centred cubic structure

Close packed hexagonal structure— The forms of Brillouin zones for this structure vary according to axial ratio and cannot be uniquely defined owing to the complexity of the structure The first zone may be regarded as bounded by $\{10\bar{1}0\}$ and {0002} planes, or alternatively by $\{10\bar{1}0\}$, {0002} and $\{10\bar{1}1\}$ planes[1] A possible next outer zone may be constructed from these three planes, together with planes of the type $\{10\bar{1}2\}$ The calculations have been carried out for the axial ratio characteristic of titanium (1 601) and the form of the zone is shown in *Figure 3* Its volume is $1\ 85/a^3$, corresponding to 2 57 electrons per atom The inscribed sphere, which

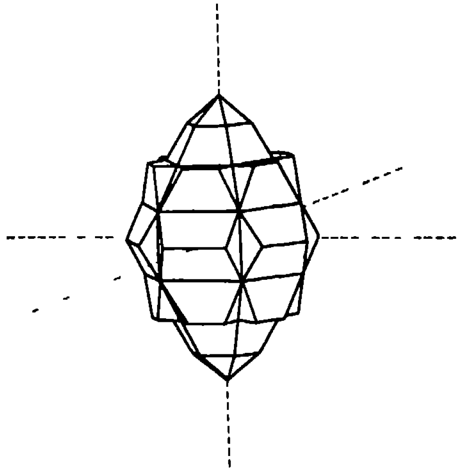

Figure 3 Outer zone for close packed hexagonal structure

touches the figure at the corners of the hexagon in the equatorial plane, corresponds to 1 75 electrons per atom It is possible that the small re-entrant portions round the equator should also be included in the second zone, in which case the volume becomes 1 89/a^3 Such a zone, however, is of limited interest for studies of titanium, which has four valency electrons per atom An outer zone corresponding roughly to this number of electrons is formed by the {10$\bar{1}$2} and {11$\bar{2}$0} planes, *Figure 4* This has the volume 3 72/a^3 and corresponds with 5 15 electrons per atom The inscribed sphere of maximum radius touches the {10$\bar{1}$2} faces and corresponds with 3 59 electrons per atom If overlap takes place here it will be into a next outer zone bounded by {10$\bar{1}$3} planes and the existing {11$\bar{2}$0} planes The inscribed sphere to this outermost zone would correspond with 5 81 electrons per atom It seems, therefore, that in considering the alloying behaviour of hexagonal titanium, the zones bounded by the {10$\bar{1}$2}, {11$\bar{2}$0} and {10$\bar{1}$3} planes may be of importance

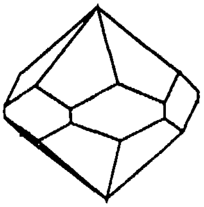

Figure 4 Close packed hexagonal zone containing 4 electrons per atom

This work forms part of a more general programme, in connection with which grateful acknowledgement is due to Imperial Chemical Industries Ltd for generous support

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Research Special Supplements

Photographic Sensitivity, *Research Special Supplement No 4*, is based on the Conference on 'Fundamental Mechanisms of Photographic Sensitivity' organized at the University of Bristol during 28–31 March In addition to a large number of papers containing hitherto unpublished material, abbreviated records will be included of the significant discussion arising at the meeting Contributors to the Sections include

Physical Properties of the Silver Halides
  R W Pohl, H Pick (Göttingen), E E Schneider (Newcastle-upon-Tyne), O Stasiw, J Teltow (Dresden), C Boussonnas (Paris and Neuchâtel), D W Pashley (London), T B Grimley, A K Holliday and K N Davies (Liverpool), G C Farnell and P C Burton (Harrow), J W Mitchell (Bristol)

Production and Properties of Silver Halide Grains in Photographic Emulsions
  T Krummenerl (Berlin), H Amman (Fribourg)

Photographic Sensitivity
  J Eggert (Zurich), H G Lowe, J E Jones and H E Roberts, B H Carroll and W West (Rochester, U S A), E E Loening (Harrow)

Latent Image Formation
  P C Burton, E E Loening, G W W Stevens (Harrow), H Bäckström (Sweden), D Sauvenier, A Hautot (Liège), J W Mitchell (Bristol), J Rzymkowski (Zagreb)

Nuclear Track Emulsions
  L Jenny (Basel), E C Dodd and C Waller, F A Roads (Ilford), L Winand (Liège), Mlle Albouy and Mme Faraggi (Paris), Miss C Dilworth (Brussels), G W W Stevens, A C Coates, R W Berriman (Harrow), M Morand and L van Rossum (Paris and Liège), J Rotblat and C T Tai (London), P H Fowler (Bristol)

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Commentary:
Mathematics in the Larger Context

One of the general principles which runs through higher mathematics is called the principle of duality: usually this is first encountered in geometry. The principle is interesting and intriguing; it is easily grasped if properly presented, and it occupies a strategic place in that region of geometry which is entered by anyone who goes beyond the isolated propositions of an ordinary school course on triangles and circles. The principle can be described in various ways: suppose, for example, that a geometrical figure is drawn upon a sheet of paper consisting of lines, points and curves disposed at pleasure. Suppose further that the figure illustrates some particular property, as that certain of its points which are apparently disconnected lie upon a straight line. Then it is always possible to draw another figure related to the first and such that for every particular point of the first there is a particular line of the second, and, further, that the second figure exhibits a related property, as that certain three of its straight lines which are apparently disconnected pass through one point. In such a case one figure is said to be the dual of the other, and the properties also that the figures represent are said to be duals of each other.

Accordingly we have two figures F and G possessing certain properties P and Q, such that when the figure F is changed into the figure G then the property P is changed into the property Q. Some definite prescription is of course needed to bring about this change of state from F to G. In the earliest instances this was done by invoking certain simple facts of circles and conic sections. For instance, as Vieta was perhaps the first to show, the figures might be spherical triangles, the lines being great circular arcs. The north pole and the equator on a sphere are 90° apart: let us say that the equator is the dual of the pole. Every point upon the surface of the sphere has its dual line 90° away from it. Mark three points upon the sphere, and they form a spherical triangle. Treating each point in turn as a pole, draw its equator; thus we have three great circles, arcs of which together form another spherical triangle, the polar triangle of the first triangle, the points of the one corresponding to the sides of the other. This is a simple example of the duality subsisting between figures F and G. Without going into technical details we may assert that one characteristic of such a pair of dual figures is the reversibility of the change from the one to the other: we may proceed indifferently from F to G or from G to F, and unless this is possible the figures are not truly dual of one another. Again, suppose that the truth of the property P is known; then that of Q can be inferred, and again this passage is reversible, from the truth of Q can be inferred that of P. To embark on this principle may indeed prove to be a voyage of discovery. Someone may assert the proposition Q of the figure G, and it may sound abstruse and strange: but it is always open to examination by the principle of duality. It translates systematically and unambiguously into a dual proposition P, which may indeed be something quite familiar. As a schoolboy I was first captivated by the method on learning from my father how an intractable problem in the

Mathematical Tripos had, to his delight, reciprocated into the well known orthocentric property of a triangle and the truth of the one implied that of the other

The next point to notice is the character of the change from F to G It is abrupt and catastrophic In this it is essentially distinct from other processes of transformation which play a prominent part both in mathematics and in the physical sciences Projection is indeed an important geometrical device which alters one figure into another, foreshortening this circle into that ellipse, lengthening this line, reducing that, but in the main never altering a point to anything but a point The gradual processes of evolution, the comparison of this shape with that, as when Sir D'ARCY THOMPSON compared two fishes, the *scarus* with the *pomacanthus*, belonging to neighbouring families, by using a conformal transformation that mapped the shape of one creature upon the other, the telescope that focuses a star cluster upon a photographic plate—all these are types of a mathematical principle which exhibits continuity, progress and differentiation within a process of change that proceeds by degrees point by point This point in figure F becomes this point upon its map M, in complete contrast to the earlier change from F to G when this point becomes that line MERCATOR contrived a rectangular map of our spherical world where admittedly two isolated points, the north and south poles, are transformed into lines, so that their neighbourhoods receive undue prominence in sheer area upon the map but this is exceptional for projective transformations Isolated points may refuse to be focused On the contrary it is universal for the principle of duality

SELF-DUALITY

We must distinguish between the change from F to G that has been described as abrupt, and the actual aspect of the figures Indeed, they may look alike they may even coincide In the case of a spherical triangle consisting of a quarter hemisphere comprised between the north pole and two points that are situated 90° apart upon the equator, the triangle would be its own polar triangle, for each of its sides is 90° away from the opposite vertex accordingly this figure is its own reciprocal, and is called self-dual, so that F and G are now the selfsame figure So far the suggestion has been that some geometrical device has been necessary for producing this duality, analogous to the use of an optical instrument which projects the object into its image But the fact that in certain instances the figure may be its own dual leads to a more abstract idea, namely that no mechanism is necessary for producing a geometrical duality , the duality may reside in the very texture of space itself and this is the view that has come more and more into prominence during the last hundred years of geometrical thought Take the triangle it is a simple affair of three points, but it is also three lines, the points constituting its vertices and the lines its sides Just as two vertices lie on one of its lines, so also two sides pass through one of its points and any such single statement cast into this form can be balanced by another statement, its dual, wherein the words ' line ' and ' point ' interchange their roles The example is absurdly simple it none the less contains the germ of a vast and wonderful system that unfolds from one dimension to another In this way we arrive at the conception of a set of propositions A, which are clear and precise , another and parallel set of propositions B, which are equally clear and precise that both sets belong to an inclusive whole that there is an interplay between them and a perfect balance that each set enriches the other, the known proposition of the one set leading to the discovery of its counterpart in the other Books of geometry have appeared with such propositions displayed in parallel columns on the same page like the old editions of Euclid with a Latin translation alongside the Greek Mathematicians are apt to take this duality for granted and not always to reflect how remarkable it is

DUALITY IN THREE DIMENSIONS

So far we have been considering duality upon a plane or a surface, two dimensional duality in fact, wherein the simplest example of a self-dual figure is the triangle But three points do not always form a triangle , they may lie in one line, and here the duality breaks down Curiously enough this exceptional circumstance lends itself to the next example of a self-dual figure, which is obtained by taking not one trio of such points, but a pair, namely ABC in one line and DEF in another line of the plane By joining these points crosswise we can obtain three new points XYZ, X where BF meets CE, Y where CD meets AF, and Z where AE meets BD It is then the case that XYZ also are in line Such a figure was known to PAPPUS, a geometer of the late Greek period (A D 300), and it is said to be self-dual It has nine points, each the meeting place of three of the lines, while it has nine lines, each containing three of these points Much could be said on the significance of this nonet the figure is fundamental for contemporary geometry The property displayed by this figure was doubtless first found out by the metrical methods of EUCLID subsequent study has shown that in systems other than that of Euclid the property continues to hold, where more familiar properties fail This suggests that it has a deeper significance To accept it as a primitive fact and then to deduce its fruitful implications which include many another well known fact is in the end a simpler procedure than to start in more traditional ways with the concepts of distance and length, for they have had to be revised and modified to suit the requirements of physics A N WHITEHEAD has described geometry as the science of cross classification, a profoundly apt description In this ninefold figure of Pappus we have a perfect symbol exhibiting this truth with emphatic simplicity, a kind of geometrical constellation of Orion

Duality gains interest as dimensions are added In three dimensions the line which was the dual of the point in two dimensions is now found to be self-dual, while the plane is the dual of the point, and *vice versa* The three vertices of a triangle are now the dual figure of the three plane faces of a corner, the three edges meeting at the point of the corner and corresponding to the three lines forming the sides of the triangle This common number three is to be expected of the lines, for in the duality line becomes line The simplest self-dual figure is now the tetrahedron which consists of four points and four planes, each plane containing three of the points and each point lying in three of the planes It also has six lines, each containing two of the points and lying in two of the planes Engineers make use of such a three dimensional duality when they draw a force diagram G to illustrate the forces belonging to a framework of light rods in equilibrium

DUALITY IN HIGHER DIMENSIONS

As one proceeds to four and higher dimensions duality persists, only it enlarges The dual of a point is not always the same thing, as we have seen, for it is a line in two and a plane in three dimensions In this way a chain of dualities is suggested, and we may envisage a nest of spaces, starting with a point within them all, then a line containing the point, then a plane containing the line, then a solid containing the plane, and so on to n dimensions within which the whole set of these items is imbedded The last but one space, which is of $(n-1)$ dimensions, is called a prime, and a prime is the dual of a point relative to these n dimensions so that a prime is a line, plane, or solid according as n takes the values 2, 3, or 4 respectively All the smaller dualities belonging to the imbedded spaces of fewer dimensions are partial, compared with the fuller duality that belongs to their all embracing space In this space there are as many primes as there are points and any geometrical figure may be analysed into its constituent points, or again and by the dual process into its constituent primes This may be illustrated in another way by considering a plane curve either as the totality of its points or as the envelope of its tangents Thus a curve may be drawn by a pen on paper pointwise it may equally well be cut out by a pair of scissors, line upon line, primewise Or, again, we may liken these analyses, the punctual and the primal, let us say, to the technique in fashioning a work of art the painting is punctual, the sculpture is primal

While it is impossible mathematically to divorce these two modes of analysis yet it is undeniably true that the one which is here called the punctual is far commoner in practice than the other The history of the physical sciences from EPICURUS to the twentieth century exhibits this The notion of elementary particles is fruitful, whether they be those of earth, air, fire and water, as the Ancients thought, or the atoms and molecules of yesterday, or the electrons and neutrons and the like In many cases it is natural to analyse a system into its constituent points , yet there are cases when the reverse is true The shapes of the bright caustics formed by reflected light are properly regarded as curves enveloped by the rays, in a primal manner The punctual analysis though equally applicable is by comparison artificial But in the realm of growth and form both analyses are significant The seed, the stem and the leaf of a plant suggest two ways of studying the three dimensional shape, the one pointwise microscopically and the other planewise

So far it has been assumed that the space is of a finite number of dimensions within which the primes exist as spaces of penultimate dimension, the relation between points and primes constituting the duality If, however, the space is of an infinite number of dimensions—such as mathematicians conceive when they speak of Hilbert space, named after the pioneer who first seriously studied it—then it is possible for this duality to break down The matter is not altogether abstract inasmuch as the technique of infinite matrices with which M Born and W Heisenberg investigated quantum mechanics leads to this mathematical concept It would take us too far afield to consider here the possibility of a transfinite duality applicable to an infinity of dimensions

DUALITY IN OTHER BRANCHES OF MATHEMATICS

From geometry the principle of duality passes to other branches of mathematics Through analytical geometry a figure can be examined pointwise by sets of numerical coordinates that must satisfy certain algebraical equations This algebraical apparatus then belongs to the figure which is its geometrical interpretation But the same apparatus, by the nature of its construction, also belongs to a dual figure, and the latter is simply obtained by a judicious interchange of the roles played by the numerical symbols that occur in the algebra Just as duality was found to be an inherent property of space, so in algebra and arithmetic it again appears as an inherent property of number A simple—but not quite obvious—numerical instance is exhibited by comparing the numbers 41532 = F and 25413 = G, each consisting of five digits Here there is a duality between the value and the position of the digit The 4 in the first place of F answers to the 1 in the fourth place of G, the 1 in the second place to the 2 in the first place, and so on Whichever of F and G is given the other may be recovered by the simple interchange of value and place

DUAL HYPOTHESES

This mathematical duality is not a case of competing theories, where one is right and the other is wrong one cannot take sides in favour of hypothesis P and against hypothesis Q, nor hold either or both provisionally until further evidence is decisive one way or the other The characteristic description of their relationship is that of in and through but not of for or against They are contemporaneous and complementary Between them there is indeed interplay, but it is not the play to win or to lose or even to draw Nor is it true that one branch of the inquiry is analytical and precise while the other is vague and dreamy each is in fact a true analysis, and its existence necessitates the other Nevertheless each can be followed for its own sake without necessarily forcing attention upon the other There is something akin to this in the story of physics during recent decades The punctual analysis that has led through the atom to the fundamental particles of matter has had to defer to another, let us say the primal, analysis that views the electron as a wave Are these to be reckoned conflicting theories that must be followed ,separately on different days of the week, as used to be said, or is it possible that both are right for deeper reasons than have yet emerged ?

The work of A N Whitehead and B Russell has led to a new understanding of the philosophy of mathematics out of which have arisen several schools of thought In one school it is held, as Russell has taught, that mathematics is fundamentally a branch of logic another school asserts that logic is part of mathematics Here appears a flat contradiction, yet in each case the conclusion has been reached by careful and exhaustive analysis A further examination of the fundamental assumptions of mathematics and of logic may some day disclose a principle of duality in a larger context, no longer within mathematics itself but including mathematics and logic as dual aspects of a richer reality

SEMANTICS

Grammar and rhetoric of old were fundamental for education. Nowadays the new science of semantics has grown, to meet a need for precision in language, and to bring to bear upon the world of letters the same penetrating analysis as that with which Whitehead and Russell explored mathematics Semantics have been elaborated in an attempt first to disclose and then to abandon unnecessary assumptions According to this discipline words being the symbols of thought have, as it were, to be sterilized in order to remove from them their allusive power This is indeed an important undertaking and it is an excellent example of a thoroughgoing punctual analysis but there is everything in mathematics to suggest that the treatment is misleading by remaining incomplete A primary approach is also needed and the existence of geometrical duality suggests how this might come about It is a fact that duality is inherent in language and at all levels, and a fruitful exploration of language is possible with this fact in view For example duality appears at the level of single words, as between the word ‘ all ’ and the word ‘ this ’ We may speak of all honest acts or again of this particular honest act, of honesty itself or of an instance of honesty Words must change to live, and a word once fixed becomes useless for purposes of art, we may add, for purposes of science also

Duality appears at higher levels than single words, as in the relationship between the pronouncements of the scientist and those of the poet, between the theorem and the proverb, between faith and works, between the letter and the spirit It appears in the contrast between the two great language systems of the Chinese and of the West The naive attitude that translation from one language to another may proceed word for word breaks down at the most elementary stage in an attempt to bridge a gulf between the East and the West The fuller understanding comes when both systems of thought are recognized as possessing the twofold character, with a different emphasis between the branches of the duality, and when the liaison is attempted between the meanings underlying the verbal expressions and not initially between the words themselves

SOCIAL IMPLICATIONS

Geographical contrast of East and West is not a relation of duality, neither is left and right for the essence of the dual relation is that of coexistence and of interpenetrability in one organic whole This duality or reciprocity is inherent in reality, and resides in the texture of the world Failure either to recognize it or to admit it leads to antagonism This has a bearing on what a German worker speaking publicly in England has recently said ‘ In 1918 in Russia the class war was fought with machine guns, artillery and aeroplanes In this second half of the twentieth century the atom and hydrogen bombs have brought a new factor into man's environment class warfare now means world war with atom and hydrogen bombs which would result in the complete destruction of East and West and the ruin and misery of all classes, most of all the workers in every nation Anti-communism merely increases the strength of the communist forces What is needed is a more powerful, satisfying and attractive ideology lived out and applied to the social, industrial and international order by everyone in the Western democracies as a prelude to bringing it to the East ’

Upon the history of the last four centuries and the present state of the world in all its turmoil and uncertainty mathematics has light to throw First it shows, in its principle of duality, the possibility of a fundamental unity that does violence to neither wing of the theory but requires them both and next it exhibits self consistency within a one-sided interpretation of circumstances which nevertheless is imperfect and still requires the richer interpretation lying outside the single wing It is a repaying adventure to step out into the larger world and with these lessons at heart to consider the relation between the individual and the community, to reflect how individualism has failed as the embodiment of a punctual analysis that ignores the primal, and how collectivism has failed being an experiment in the primal analysis that ignores the personal and then to reflect how a unity which includes them both has been discovered in the more excellent way that illumines the things within, in the heart, and without, in the world.

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Conduction Electrons in Non-Metallic Solids

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KNOWLEDGE of the behaviour of conduction electrons in non-metals is of importance for a variety of purposes, for instance, in connection with semi-conductors, photoconducting insulators and dielectric breakdown. It is only recently, however, that an understanding of the more basic properties has been gained, and there seems to exist considerable uncertainty as to the way in which electrons in such substances should be imagined to act. In the present review it is hoped to clarify some of the more elementary problems.

All substances with which we are concerned here are non-conductors when in the ground state. They conduct, however, when electrons have been brought into the so-called conduction levels either thermally or by some ionizing radiation or through the influence of a strong electric field. These electrons may emerge from lower energy levels of the pure substance, or they may be closely connected with the existence of lattice defects or admixtures of foreign atoms in minute concentration. Questions relating to ionic crystals have been discussed by N F MOTT and R GURNEY[1].

In the conduction levels electrons would behave very nearly like free electrons if their interaction with the material and with each other could be described by a periodic potential field; the only alteration then required would be the replacement of electronic mass by an 'effective' mass. To find the actual behaviour we must thus look for deviations from strict periodicity, due either to *1* displacement of ions and atoms of the lattice or *2* interaction with other electrons. *2* will naturally be of considerable importance if the density of conduction electrons is comparatively high. In the following we shall thus consider first some properties of individual electrons in pure substances; secondly, as an example of cooperative properties, we shall investigate some processes in which the number of conduction electrons varies with time.

SLOW ELECTRONS IN IONIC CRYSTALS

In this section we shall investigate the properties of electrons in perfect ionic crystals in a concentration so low that collisions between electrons become unimportant. Deviations from the behaviour of free electrons arise from interaction between electrons and from displacements of the lattice ions; such displacements can either be spontaneous due to thermal motion, or they can arise out of the interaction with electrons. The former leads essentially to thermal scattering, the latter to a (negative) energy of interaction which shifts the energy levels of free electrons to lower values.

It is characteristic of ionic crystals that any displacement of charges is opposed by restoring forces. In contrast, dipolar substances usually contain molecular dipoles with several equilibrium positions in the lattice. The restoring forces in ionic crystals lead to oscillations in two main frequency ranges: an optical range, corresponding mainly to displacement of bound electrons and a range usually corresponding to frequencies of electromagnetic radiation in the far infra-red. We shall be mainly concerned here with the latter range; the frequencies refer to displacement of ions, including such electronic displacement as is coupled with this.

Moving point charge in ionic lattice.— To study now the reaction of the enforced displacement of ions on the motion of an electron, consider an ionic lattice at the absolute zero of temperature, where no thermal vibrations are excited. Also, as an introduction, let us first investigate the effects of a point charge moving with constant velocity v through the lattice[2,3]. Ions at very large distances from this charge will be displaced, as with a static charge; at short distances, however, they will not in general have sufficient time to carry out the complete static displacement. If ν is the frequency of oscillation of an ion it takes about $1/\nu$ sec to complete the static displacement; thus, roughly speaking, ions will be displaced adiabatically, as with a static charge, if their distance from the charge is larger than v/ν. For shorter distances the interaction takes the form of a shock, and energy is transferred to the ions. It follows that the point charge carries with it a polarization the potential of which is approximately equal to the static potential at distances beyond v/ν but which remains approximately constant for shorter distances. The change of energy due to this polarization is therefore of the order

$$-\frac{e^2\nu}{v}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon}\right) \qquad (1)$$

where ε is the static dielectric constant and $\sqrt{\varepsilon_\infty}$ is the optical refractive index, provided that v/ν is larger than the lattice distance. The interesting feature in expression 1 is the proportionality of the energy of interaction with $1/v$. A further point of interest arises from the quantization of the ionic oscillators. the point charge can emit energy to these oscillators only in quanta of energy $h\nu$.

Moving electron in ionic lattice—The above considerations need be altered only slightly if applied to a fast electron rather than to a point charge, provided that the de Broglie wavelength h/mv is small compared with v/ν; it then excites the same displacements in the lattice as does a point charge. In view of the recoil from the emitted quanta $h\nu$, however, it is scattered into a different direction in every emission process. The connected change in momentum can be considerable, but the energy changes only by $h\nu$, which on the present assumption ($h/mv \ll v/\nu$) is small compared with the kinetic energy. This scattering is thus nearly elastic.

Consider now the example of much smaller electronic velocity, i.e. of much larger de Broglie wavelength. The above considerations break down whenever the de Broglie wavelength surpasses the critical distance v/ν since the electron cannot be considered fixed in a range smaller than $h/mv > v/\nu$. One might tentatively try to replace v/ν in (1) by h/mv, leading to an interaction energy of the order

$$-\frac{e^2mv}{h}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon}\right) \qquad (2)$$

Clearly a minimum energy (largest magnitude) would then be reached when $h/mv \simeq v/\nu$. Its value is of the order W where

$$W=\frac{1}{2}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon}\right)e^2\left(\frac{m\nu}{h}\right)^{\frac{1}{2}} \qquad (3)$$

This result is confirmed by recent calculations[4] on the lowest energy levels in a range $h\nu$ above the ground level, using a variational method. Restriction to a range $h\nu$ simplifies the mathematical treatment, since emission of quanta $h\nu$ is then impossible. For a given total momentum of the system 'electron plus ionic displacements' it is found that the wave function describing such a state consists of a superposition of functions in which the electron and ions share the momentum in various ways. In the lowest state, for instance, the total momentum and the average velocity $\bar{v}$ of the electron vanish. The kinetic energy of the electron, proportional to $\overline{v^2}$, does not, however, vanish.

The decrease E_0 in the energy of free electrons due to interaction is found from the equation

$$E_0(E_0+h\nu)^{\frac{1}{2}} = W(h\nu)^{\frac{1}{2}} \qquad (4)$$

This means that $E_0 \simeq W$ if $W < h\nu$, and $E_0 \simeq W^{\frac{2}{3}}(h\nu)^{\frac{1}{3}}$ if $W \gg h\nu$.

Although interaction may depress the energy considerably, compared with $h\nu$, it was found that this decrease is nearly independent of the average electronic velocity $\bar{v}$. It follows that for our system the dependence of energy difference from ground level on $\bar{v}$ is practically the same as for free electrons.

Polarization of medium—To clarify further the properties of this system it is of interest to investigate the polarization of the medium. The average polarization vanishes, since the electron can be found with equal probability at any point in the medium. This does not hold, however, for a more interesting quantity, the average polarization at a given distance from the electron, wherever the latter may be found. In the ground state the latter can be derived from a polarization potential P shown in *Figure 1* as a function of the distance x from the electron. At large distances and down to distances of the order $(h/m\nu)^{\frac{1}{2}}$ it behaves like that of a point charge. At shorter distances however deviations occur of a type similar to those for a moving point charge; these are due to the motion of the electron, which leads to the above mentioned kinetic energy, even in the ground state.

The above discussion of polarization holds in the first place for the ground state in which the average electronic velocity $\bar{v}$ vanishes, in contrast to the average kinetic energy. In higher levels where $\bar{v}$ no longer vanishes we should expect little change so long as $\bar{v}$ is sufficiently small; in fact we should expect an appreciable alteration only if $\bar{v}$ is so large that $\bar{v}/\nu$ becomes larger than the range $(h/m\nu)^{\frac{1}{2}}$.

It is now understandable that the energy of interaction depends so little on the average electronic velocity $\bar{v}$; this energy is equal to the product of the charge e and the value of P at the electron position, i.e. at zero distance, the latter varying only slowly with $\bar{v}$.

Self trapping—Let us assume with L. LANDAU[5] that an electron has remained for some time in a small region in the medium. This region produces a certain average potential which in turn if acting on the electron would attract it, giving rise to a bound energy state[1]. Such a procedure can be made self consistent[6, 7]; it then represents an approximative calculation of the energy of

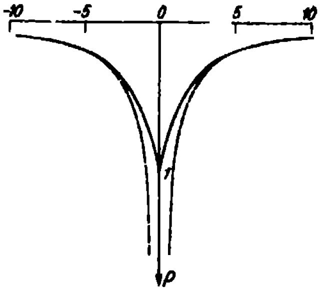

Figure 1 Polarization potential P as a function of distance x from the electron. The broken line refers to a point charge

interaction E_r in an approximation of a different type from that used in (1) Results by S PEKAR[6] give

$$E_r = -\frac{0.164me^4}{(h/2\pi)^2}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon}\right)^2 \qquad (5)$$

instead of equation 4, which shows that

$$\frac{|E_r|}{W} = 0.33\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon}\right)\frac{b}{a_0} \qquad (6)$$

where $a_0 = h^2/4\pi^2me^2$ is the Bohr radius, and $b = (h/8\pi^2m\nu)^{\frac{1}{2}}$ is the length already introduced. It shows that as long as $W < h\nu$ the previous method gives the lower energy This is not astonishing because the last method would be a bad approximation if the extension of the 'bound state' were larger than the range within which displacement does not immediately follow the electron This would result in replacement of the actual polarization potential by its average value even outside this range, hence the method would lead to too high values of potential energy The same holds of the kinetic energy because the electron is fixed within a certain region when it should be with equal probability anywhere in the medium For values of $W > h\nu$, however, the approximation is much better for sodium chloride it gives a value[7] of electron energy even slightly larger than does the previous method—0.13 and 0.09 ev respectively

To obtain self trapping two objectionable assumptions have to be made in connection with the Landau method

a It must be assumed that the whole configuration connected with a 'bound state' cannot move rather freely through the medium This would be at variance with the results discussed previously according to which our system has nearly the same inertia as a free electron Without proof assumption *a* is usually justified by the heavy ionic mass However, to move the electron cloud through the medium requires mainly a displacement of the ions outside the main extension of the cloud We have seen that this should be easily possible if the average velocity $\bar{v}$ is so small that $\bar{v}/\nu$ is smaller than the extension of the cloud It seems, therefore, that there is no justification for assumption *a*

b According to the second assumption there should be a continuum above the (presumed) discrete ground level similar to that of an electron moving in a permanent field of force In this latter example an electron with an energy in the continuum must have sufficient kinetic energy to move out of the range of the force It thus happens that the energy of the bottom of the continuum is identical with the lowest energy found in the approximation in which interaction energy is neglected In our example of self induced potential an electron can never escape from the field of force except by moving very fast (The mistake usually made is to apply the Landau method to an infinitely extended electron cloud which would lead to zero interaction energy Here, however, the method completely breaks down, for its validity implies that the displacement of any ion is not altered while the electron moves through its orbit)

It follows that in assumption *b* the difference between the energy in two different approximations is confused with the energy difference between two states We thus conclude that self trapping cannot exist

Mean free paths— If an electric field F is applied to a dielectric medium containing electrons, an electric current $\imath$ results which is proportional to F up to very large field strengths This current should also be proportional to the number n of electrons per unit volume If thus we separate off a further factor e^2/m and write

$$\imath = \frac{e^2\bar{\tau}nF}{m} \qquad (7)$$

the quantity $\bar{\tau}$ has the dimensions of time it will be called the average time of relaxation It has so far only been possible to calculate $\bar{\tau}$ when interaction between electron and medium can be considered as a small perturbation This includes fast ($\gtrsim$ 1 ev) electrons, and in some substances also electrons with energy less than $h\nu$ above the ground level Here the interaction between an electron and the medium can be described as absorption or emission of quanta $h\nu$ by the electron connected with a change of its momentum (scattering) $\bar{\tau}$ is then the average value over all electrons of the relaxation time τ_E which refers to a single electron with energy E Both $\bar{\tau}$ and τ_E may depend on temperature The relaxation time τ_E is closely correlated with the average time between two collisions i e absorption or emission of a quantum, it also contains, however, a factor giving different weight to collisions according to the scattering angle

Instead of the relaxation time τ_E the mean free path defined by $l_E = \tau_E v$ is often introduced Roughly it represents the average distance which an electron travels before being deflected by an appreciable angle

A calculation of the mean free path[8] for electrons with velocities of several ev gives values of the order of 10^{-6} cm which increase proportionally with the square of the energy Below an energy of the order of 1 ev this changes into first order proportionality with energy Formal application of perturbation theory in this region leads to a simple result[4], namely,

$$\frac{1}{l_s} = \frac{1}{l_0}\left[1 + \frac{2}{\{\exp(h\nu/kT) - 1\}}\right] \quad .(8)$$

where

$$l_0 = 2\,\frac{\varepsilon\varepsilon_\infty}{\varepsilon - \varepsilon_\infty}\,a_0\,\frac{E}{h\nu} \quad (9)$$

On the assumption that perturbation theory is applicable this equation should hold for energies E above several $h\nu$ up to about 1 ev In thermal equilibrium at temperatures $T \gg h\nu/k$ most electrons have energies above $h\nu$ Then the average mean free path follows from equations 8 and 9 as

$$\bar{l} = \frac{3}{2}\,\frac{\varepsilon\varepsilon_\infty}{\varepsilon - \varepsilon_\infty}\,a_0 \ , \quad \text{if} \quad kT \gg h\nu \quad (10)$$

This leads to values of $\bar{l}$ of the order of 5×10^{-8} cm, which is much smaller than the de Broglie wavelength of thermal electrons We have thus to conclude that interaction in this energy region is so strong that the perturbation method is no longer applicable

For most polar materials the frequency ν is so high that temperatures below $h\nu/k$ are of greatest interest most electrons then have energies less than $h\nu$ above the ground level From the point of view of perturbation theory they have insufficient energy to emit quanta $h\nu$ but they can, of course, absorb them Scattering probability is then proportional to the density of free quanta $h\nu$ in the material This leads to a temperature dependence of the mean free path

$$l_s = l_1\{\exp(h\nu/kT) - 1\} \qquad h\nu > kT \quad (11)$$

instead of that of equation 8 The frequency ν is that of long longitudinal polarization waves it can be obtained from the frequency ν_r of residual waves, which is known experimentally, by

$$\nu = \nu_r\left(\frac{\varepsilon}{\varepsilon_\infty}\right)^{\frac{1}{2}} \quad (12)$$

A calculation of l_1 has been given some time ago[9] but has to be modified in view of more recent developments[4] This leads to

$$l_1 = 3\,\frac{\varepsilon\varepsilon_\infty}{\varepsilon - \varepsilon_\infty}\left(\frac{E}{h\nu}\right)^{\frac{1}{2}} a_0 \quad (13)$$

In thermal equilibrium it is then found that

$$\bar{l} = \frac{6}{\sqrt{\pi}}\,\frac{\varepsilon\varepsilon_\infty}{(\varepsilon - \varepsilon_\infty)}\left(\frac{kT}{h\nu}\right)^{\frac{1}{2}} a_0\,\{\exp(h\nu/kT) - 1\} \qquad \text{for } kT \ll h\nu \quad (14)$$

Agreement with experiments on cuprous oxide[10] which was discussed previously[9] is improved by this new formula These experiments give a value of $l = 25 \times 10^{-7}$ cm at 80°K which drops to a constant value of 6×10^{-7} cm at 200°K and higher temperatures. This temperature dependence can be accounted for by putting $h\nu/k = 280$°K in equation 14, giving almost half the experimental value, which seems very satisfactory It is also of interest that above 200°K the mean free path is independent of temperature, as would also follow from equation 10 The absolute value of $\bar{l}$ following from this formula is, however, much too small This indicates that the transition from the temperature dependence, equation 14, to the temperature independent region occurs at lower temperatures than would follow from perturbation theory

Finally it should be remarked that non-polar substances behave very differently from polar ones. The mean free path of the latter is proportional to $1/T$ down to very low temperatures It has a magnitude considerably larger than for polar materials so long as $kT > h\nu$ for the latter This can be concluded from equation 10 although the mean free path is unlikely to be as small as would follow from this formula Below $T = h\nu/k$, however, when equation 14 holds, the mean free path in polar substances increases much more rapidly, being proportional to exp $(h\nu/kT)$ than in non-polar ones, when it is proportional to $1/T$ This behaviour is due to the decrease in excitations of the polar vibrations

It must be pointed out in this connection that even in polar substances there is always a certain amount of non-polar scattering From the above it follows, as has been pointed out by F SPITZ[11], that above or near temperatures $T \sim h\nu/k$, non-polar contributions can be neglected if $T \ll h\nu/k$, however, they should become important in view of their slower increase with decreasing temperature

$$\frac{1}{l} = \frac{1}{l_{\text{polar}}} + \frac{1}{l_{\text{non polar}}} \quad (15)$$

In the above example of cuprous oxide it appears that the influence of non-polar scattering is not very strong at 80°K ; it would be of interest to look for it at lower temperatures At very low temperatures, however, a further temperature independent term l_{foreign} due to scattering on crystal imperfections or foreign admixtures becomes important (assuming the number of imperfections to be independent of temperature) Thus

$$\frac{1}{l} = \frac{1}{l_{\text{polar}}} + \frac{1}{l_{\text{non polar}}} + \frac{1}{l_{\text{foreign}}} \quad (16)$$

In the most general case, the temperature dependence of the mean free path of electrons in a polar substance, the law given by equations 17 and 18 follows

$$\frac{1}{l} = \frac{c_1}{\{\exp(h\nu/kT) - 1\}} + c_2T + c_3 \ , \quad kT \ll h\nu \quad . (17)$$

and

$$\frac{1}{t} = c_4 + c_5 T + c_6 \quad , \quad kT \gg h\nu \tag{18}$$

where the *c*'s are independent of temperature

TIME DEPENDENT PROCESSES

Recombination— Amongst the questions of interest in connection with the behaviour of electrons in dielectric substances some do not require a detailed knowledge of the properties of single electrons but are rather concerned with the whole assembly of electrons In this section we shall deal in particular with processes in which the number of electrons contributing to conductivity changes with time[18] This takes place, for instance, after an ionizing radiation has passed through the substance and has transferred a number of electrons into levels in which they can contribute to the conductivity (conduction levels) Ultimately these electrons will return to lower levels but the manner in which they can get rid of their energy of excitation has been a puzzle for some time One possibility, which occurs in phosphors, is the emission of light ,In other materials (non-phosphors) one might think that an electron transfers its energy directly to the lattice vibrations when jumping from an excited to a lower level This would involve the simultaneous emission of a large number of vibrational quanta and thus is very unlikely

We shall discuss here another possibility, namely that in the first place the energy is transferred to another excited electron which thus acquires a high energy within the conduction levels It can then get rid of some of the energy quickly by emission of single quanta in the way discussed in the previous section Alternatively, since collisions between excited electrons are rather frequent, the electron may first share its energy with others If in particular these collisions are much more frequent than collisions with lattice vibrations it will be possible to attribute an independent temperature T_e to the electrons The above process then implies an increase of electronic temperature T_e over the lattice temperature T, which in turn leads to an energy transfer from electrons to lattice It can be shown that this transfer is a sufficiently fast process, so that it is principally the recombination which determines the rate of transfer of excitation energy to the lattice

It will be noticed that the recombination processes considered in the above model are the inverse of the excitation of an electron in a low level by an electron the energy of which above the bottom of the conduction levels is larger than the excitation energy It follows that owing to these two types of processes equilibrium will be approached A more detailed analysis shows that N, the number of electrons in the excited levels, satisfies the differential equation

$$\frac{\tau_c}{N}\frac{dN}{dt} = 1 - \left(\frac{N}{N_T}\right)^{(a-1)} \tag{19}$$

where N_T is the value of N in equilibrium at the temperature T The value of the constant a is either 2 or 3, depending on whether the number of lower levels into which the electron decays is much larger or about equal to the number of electrons[1] The above equation can easily be integrated considering an initial value of $N \gg N_T$ The decay time is then principally determined by the magnitude of the quatity τ_c which is found to be approximately given by

$$\tau_c \simeq 0\ 1\ \tau_0 \exp\left(\frac{U}{kT}\right) \tag{20}$$

Here U is the smallest excitation energy and τ_0 is the average time required by an electron with sufficient energy to excite an electron from the lower levels For $U \simeq 1$ ev, $\tau_c \simeq 10^{-8}$ seconds since, however, exp (U/kT) is a very large factor, τ_c increases very rapidly with U Thus $U \simeq 1\ 5$ ev gives $\tau_c \simeq 10^4$ sec It would seem therefore that reasonable decay times are found unless the excitation energy is much larger than 1 ev

In applying the above consideration to actual examples it must be remembered that most substances contain an appreciable number of lattice defects or other imperfections near which electrons can be trapped Frequently, then, the electrons will ultimately be transferred to these traps although they may have been removed by the ionizing radiation from other (lower) levels It must also be considered that recombination may occur in steps if there are discrete excited levels between the lower level and the continuum of conduction levels this would influence the form of equation 19 It seems, however, that τ_c would still represent a correct order of magnitude if U is the energy of the lowest excited level

The mechanism described above should lead to reasonable decav times whenever the main gap U for recombination is not much larger than 1 ev. This holds in many cases for the lowest excitation energy of trapped electrons Details of the mechanism will in general be more complicated Assume, for instance, that the primary radiation has removed electrons from low energy levels in the atoms or ions of the crystal, at first, recombination from higher levels will occur by the Auger effect i e ejection of outer electrons into the conduction levels The gap created in an outer shell may again be closed by

Auger effect until finally we are left with a number of electrons in the conduction levels which can transfer their energy to the lattice vibrations and recombine into traps in the way described above

Field dependence of electronic current— Electrons can be transferred to the conduction levels not only by an ionizing radiation but also by strong external fields[13, 14] Consider, for instance, the model mentioned above in which it is possible to attribute a separate temperature to the electrons in conduction levels Under the influence of the field, energy will be transferred to these electrons, leading to an increase of electronic temperature T_e over the lattice temperature T until equilibrium is reached by transfer of energy from the electrons to the lattice vibrations As a next step the increase of temperature of the conduction electrons will upset their equilibrium with the electrons in lower levels until not only the energy distribution but also the number of conduction electrons is increased to the number corresponding to the electronic temperature T_e The time required for this latter process should be equal to the probability of finding an electron with energy above the lowest conduction level to excite a bound electron multiplied by the time τ_e It is thus equal to the time τ_e, equation 20

It follows that the two processes, increase of electronic conductivity by a strong field and decay of conductivity after excitation by an ionizing radiation, should be governed by the same time constant It would be interesting to test this conclusion experimentally

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Activation Processes in the Sensitiveness of Explosives

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EXISTING physicochemical theories about activation processes have been developed on the basis of chemical reactions which can readily be investigated in the laboratory With most explosives conditions can be found under which thermal decomposition takes place quietly Under such conditions, the chemical energy is released only gradually and the ordinary features of chemical reactions are observed As might be anticipated with the complex molecules involved, the thermal decomposition of many explosives is monomolecular There is also a tendency with many explosives for autocatalysis of the decomposition by the reaction products

Explosives can however release their chemical energy with progressive violence under the action of various external stimuli Special difficulties arise in the physicochemical elucidation of the various mechanisms for such progressive energy release

Comparative values of the stimulus required to initiate progressive decomposition and explosion in various explosives are used to establish 'scales of sensitiveness' In any particular scale of sensitiveness, the explosives are arranged in order of magnitude of the stimulus required for explosion The need for proper safety precautions in the handling of explosives has led to the development of tests on sensitiveness using a wide variety of stimuli Most of these tests on sensitiveness are however designed to match practical conditions as closely as possible Such applied scales of sensitiveness do not lend themselves readily to physicochemical interpretation of the processes involved in the progressive energy release of explosives

Basic research on the activation processes involved in the progressive energy release from explosives suffers from the further limitation that when the quantities of material involved are at all large, special precautions are required which are not feasible in most ordinary laboratories This has to some extent restricted the range of research carried out on explosives A number of investigations have, however, been published recently[1-5] which have led to the elucidation of various physicochemical mechanisms of energy release

All explosives liberate heat when they decompose As was pointed out long ago by J H VAN'T HOFF (quoted by W. JOST[10]) any exothermic chemical reaction with positive temperature coefficient auto-accelerates when the rate of production of heat in the system becomes greater than the rate of removal of heat The conditions for 'self-heating' of an explosive are of decisive importance in determining whether any local decomposition which is started in a mass of explosive will lead to auto-accelerated transformation of the whole mass Self-heating is not peculiar to explosives, since it can occur for any exothermic reaction, and can be discussed without specific reference to the activation processes involved[9, 10]

Problems which are specific to the sensitiveness of solid and liquid explosives include

1 The processes whereby various stimuli such as impact, friction or electric sparks can trigger 'local decomposition' from which self-heating may spread.

A convenient nomenclature is to refer to these local decompositions as 'hot spots' The physicochemical problem is to determine how 'hot spots' originate when explosives are subjected to various types of mechanical and other stresses In particular, it is important to establish whether these stresses merely lead to local rise of temperature with subsequent random transfer of activation energy, or whether they can lead to chemical activation by non-random processes of energy transfer

2 The possibilities of non-thermal activation of molecules in contiguous layers around a hot spot

The most obvious mode of growth of a 'hot spot' is through the heating of contiguous layers by ordinary processes of heat transfer In solid and liquid explosives conduction of heat is of predominant importance owing to the high kinematic viscosity So far as this process is sufficient to account for the phenomenon of sensitiveness, the thermal activation involved is not specific to explosives and does not call for special comment Definite examples of non-thermal activation of molecules in contiguous layers, so far as they are known, are discussed below

3 The special physical chemistry of reactions in the detonation wave

A basic distinction arises between auto-accelerative chemical decomposition due to self-heating, and chemical activation of molecules in the detonation wave The growth of hot spots in a self-heating mechanism is a comparatively slow process, conditioned by the heat of decomposition and thermal conductivity of the explosive In detonation, chemical decomposition occurs much faster, and at much higher temperatures and pressures. So far as they have been elucidated, activation processes in detonation are discussed below. Physical factors such as rates of volatilization and diffusion appear to be of controlling importance

TRIGGER MECHANISMS IN THE PRODUCTION OF HOT SPOTS   TRIBOCHEMICAL ACTIVATION

When a given mass of explosive is subjected to the impact of a falling weight, to mechanical friction or to an electric spark, it is usually possible to calculate the rise of temperature of the explosive from the energy dissipated in the stimulus applied The electric spark presents special problems and will not be discussed further here In impact sensitiveness, if the energy of impact were dissipated uniformly throughout the explosive, the rise of temperature would normally be wholly inadequate to account for the explosion, as can be verified directly by warming the same mass of explosive to the calculated temperature Observed explosions must therefore be due either to the fact that decomposition is accelerated in some way at the momentarily high pressures due to the blow, or to the fact that the energy of impact can be concentrated in some way at local 'hot spots'

Various specialized experimental conditions have been realized in which the mode of origin of the 'hot spots' due to mechanical action on the explosive can be followed more closely than is possible in the rather crude 'falling weight' tests of sensitiveness

In liquid explosives, the presence of minute bubbles of gas gives rise to a form of impact sensitiveness, which can be directly attributed to the rise in temperature of the gas bubbles by adiabatic compression due to the impact[8]

In solid explosives, there is reason to suspect that adiabatic compression of interstitial gas may contribute to impact sensitiveness, but published experimental evidence is less definite A particularly clear mode of origin of hot spots due to mechanical action is revealed when particles of grit are mixed with the explosive[1, 3] Calculations show that dissipation of the impact energy leads to local heating around the grit particles, to an extent sufficient to account for self-heating leading to explosion Measurements on the time of development of such hot spots into explosions[4] substantiate this explanation of grit sensitiveness It is interesting to note that if inert substances such as wax or organic liquids are mixed with the explosive, the growth of hot spots can be inhibited before they build up into explosions Such 'phlegmatizers' do not appear to lessen the formation of hot spots, but by their heat capacity they increase the minimum stimulus required to start progressive energy release This application of phlegmatizers is of the greatest importance *e g* in permitting the use of the very sensitive explosive nitroglycerin in commercial explosives such as blasting gelatin Both the above mechanisms of hot spot formation involve the complete randomization of the mechanical energy of impact or friction into heat, which then leads to the familiar thermal activation of molecules of the explosive around the hot spot

In less simple instances of impact and friction sensitiveness, the possibility must still be considered of the activation of molecules of the explosive by *some process of non-random transfer of mechanical* energy to the chemical bonds[8]

Two non-random processes which have been proposed at various times are the breaking of chemical bonds when crystals of explosive are broken[7] and the shearing of liquid (plastic) explosives at such high rates of flow that local stresses suffice for the breaking of chemical bonds The latter possibility appears to have been first suggested in a rather confused way by G TAMMAN and C KRÖGER[8]

Considerations of chemical crystallography indicate that mechanical stresses are unlikely to break *chemical bonds in crystals of low lattice energy, in* which the molecules are held together only by residual forces and in which stresses can be relieved by intermolecular movement With the ionic lattices *e g* of initiators such as lead azide and lead styphnate, *breaking of the crystals should in principle lead to a* chemical activation Examination of the relationship between mechanical and thermal processes of initiation indicates[8] that 'tribochemical' processes for the production of hot spots are probably effective *in relation to sensitiveness to impact, friction and* percussion of explosives such as lead azide At present, however, the proof of a non-random transfer of mechanical energy in the activation of chemical bonds rests on an elimination of the ordinary processes *of activation due merely to a local rise in temperature* Non-random transfers are probably also effective in the detonation wave (see below)

The possibility of direct transfer of mechanical energy into chemical bond activation without prior degradation into heat would not reveal itself very readily except in explosives This is because of the peculiarity of explosive systems which permit the 'development' of minute hot spots into macroscopic phenomena Other physicochemical systems can however be suggested in which the direct transfer might be investigated For example, silver salts might be activated by mechanical stresses and the activation could then be developed in the usual way Again, the formation of nuclei for crystallization from liquids, and for other phase changes, can be favoured by certain types of mechanical action in which the activation is properly tribochemical and not merely thermochemical

NON-THERMAL GROWTH OF HOT SPOTS

Once local decomposition of molecules has been 'triggered' by a process which may involve either random or non-random transfer of mechanical to activation energy, the question arises as to whether the 'hot spots' produced will grow or merely die out

Various examples, where the growth is conditioned by the heat of decomposition, thermal conductivity and density of the explosive system, are amenable to the self-heating theory[9, 10] For example, for a semi-infinite slab of explosive of thickness $2d$ the heating will be non-stable and will lead to explosion when

$$(d^2W/k)\{A\exp[-E/RT_0]\}(E/RT_0^2) > 0.88$$

where W = heat of reaction per unit volume, k = thermal conductivity of the explosive, $A\exp[-E/RT_0]$ = rate of decomposition, E = activation energy controlling the rate of decomposition, T_0 = initial temperature before self-heating is appreciable

So far as the experimental verification of this equation can be made, it agrees with various experimental measurements on grit sensitiveness[3, 4] The Frank Kamenetzky equation has also been followed in considerable detail for lead azide surrounded by inert media such as liquid paraffin It is interesting to note that as the density of an explosive is increased so also is increased the mass of the hot spot which must be raised to a critical temperature to ensure progressive energy release At sufficiently high densities the magnitude of the local mechanical action required may no longer be feasible and this may explain the 'deadening' of certain explosives when they are pressed to high densities[11]

In addition to problems raised by the thermal growth of hot spots, as determined by the physical and chemical variables indicated in the Frank Kamenetzky equation, the question of non-thermal growth of hot spots must be considered, particularly in relation to initiators such as lead azide

With lead azide (as with many other explosives) it is possible to follow the decomposition processes which precede detonation, by measuring the 'induction period' Υ when crystals of lead azide are suddenly warmed to any particular temperature The duration of the induction period depends upon an activation energy E according to the familiar equation

$$\Upsilon = A\exp(-E/RT) \quad . \qquad (1)$$

where A is a constant which ranges from 10^8 to 10^{14}

and E ranges from 23 to 62 kcal/mol according to the physical and chemical environments of the crystallites. By suddenly cooling the crystals during the induction process it can be verified after a time $t_1 < \Upsilon$ that they are in part transformed to metallic lead during the induction period. After cooling, if the partly decomposed crystals are brought back again to the original temperature of decomposition, the ensuing induction period t_2 before detonation practically corresponds in duration with the incomplete part of the original induction period[11] i.e. $t_2 \approx \Upsilon - t_1$.

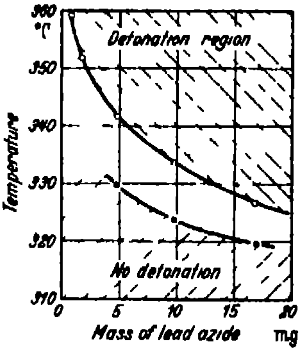
This very interesting observation implies that the partly decomposed crystals have undergone a more or less permanent sensitization to heat. Probably this can be attributed to the formation of interfaces between lead azide and metallic lead which facilitate further decomposition. A further implication of this experiment is that any heat evolved during the induction period can be dissipated without substantially affecting the duration of the delay to detonation. Under these conditions the build up of a trigger reaction into detonation of lead azide must follow a mechanism which does not depend on self-heating. Lead azide is photosensitive, and exposure to sunlight brings about sensitization which also shortens the induction period on subsequent heating. The crystals blacken on exposure to light, but the region of deposition of lead in the crystals does not appear to be quite the same as for thermal decomposition. Detailed discussion of the nature of the non-thermal mechanisms of build up of detonation in lead azide cannot be developed here. Two further comments can, however, be made. In the first place, explosions in the gas phase which are not due to self-heating can be explained in terms of a well known process of branching of reaction chains. It seems not unlikely that in crystalline lead azide a process of autocatalysis prevails which is formally analogous to chain branching in the gas phase. On the assumption that the process of thermal decomposition involves two types of reaction *a* the formation of fresh nuclei of metallic lead at random points in the lattice *b* the growth of lead nuclei already present it is not difficult to construct reaction kinetics which are auto-accelerating, and in which the state of decomposition after heating for part of the induction period would be 'frozen in' on cooling, as is actually observed.

The second comment about the build up of detonation in lead azide by a non-thermal mechanism is that this build up involves cooperative action from separate crystallites. Various lines of experimental evidence throw light on the nature of this cooperative build up.

THRESHOLD MASS AND DETONATION WAVES

At any temperature, it is found that the induction period Υ which precedes detonation follows equation 1 above, in which the numerical constants are practically independent of the mass of lead azide under investigation, at least when this ranges from about 2 to 20 mg. But as the mass is progressively reduced, a proportion of the samples fails to detonate at all. At any given temperature, the threshold mass for 50 per cent of the samples to detonate can be established with fair precision.

Figure 1 illustrates the kind of relationship between threshold mass and temperature for crystalline lead azide.



Courtesy Royal Society

Figure 1 Relationship between threshold mass and temperature for crystalline lead azide ○ *crystals, bulk density* 1·98 *gm/cc,* ● *powder, bulk density 1·90 gm/cc*

Experiments show that if the grains are separated by inert material, such as powdered glass, the threshold curve moves towards higher masses. On the other hand, if the air between the interstices is replaced by dense organic fluids such as butyl phthalate, the threshold curve is superseded by another threshold curve associated with explosion by self-heating[12]. Some kind of cooperation between the grains always appears to be required for detonation to ensue.

This phenomenon of 'cooperative build up' of detonation deserves special comment. In the self-heating mechanism, contiguous crystallites of explosive cooperate in the build up of explosion by pooling their heats of decomposition. When the non-thermal mechanism prevails, the theory proposed is that individual crystallites cooperate in producing a detonation wave by pooling the gas flow outwards which arises from their thermal decomposition. Just as in optics the wavelets from a series of diffraction centres cooperate to produce a Huyghens wave front, so the idea is that the gas streams from the individual crystallites cooperate to form the gas stream which maintains the shock wave. When this shock wave attains sufficient intensity it can activate the crystallites in successive layers by a mechanism discussed in the next section, and detonation ensues.

Special problems of activation arise in connection with the chemical processes occurring in a detonation wave. To discuss these, it is useful to contrast the process of propagation of a flame in a self-heating explosive mixture with the process of propagation of detonation. No serious restriction is introduced by considering the two processes moving down a cylindrical tube with a uniform velocity.

With the flame, its front activates molecules in the contiguous layer of unreacted mixture, in part by heat transfer and in part by the actual diffusion forward of free radicals and 'hot molecules'. These two processes of activation do not differ in any special way from ordinary physicochemical activation. The heating up of contiguous layers increases the number of activated molecules in thermal equilibrium, and the diffusion forwards of free radicals corresponds to the propagation of activation in chain reactions. The velocity of movement of such flames may range from a few metres to about 200 metres per second maximum. Owing to the fact that the reaction products are at a higher temperature and usually involve a greater number of molecules per unit mass than the unreacted system, the hot gases stream away behind the flame front[10].

In detonation, the velocity of the detonation front is much faster. For example, solid TNT at a density of about 1·5 gm/cc has a detonation velocity of about 7,000 m/sec. Increases in temperature and pressure in the detonation front are conditioned by the hydrodynamic requirements for propagation of detonation. In TNT at a density of 1·5 gm/cc the temperature T is about 2,900°K and the pressure about 10^5 atmospheres[14]. A further speciality about detonation is the maintenance of a streaming velocity V towards the head of the detonation wave. Standard hydrodynamic theory gives as order of magnitude of this streaming velocity[15]

$$V = (8{,}310T/\gamma M_2)^{\frac{1}{2}}$$

where M_2 is the average molecular weight of the products of detonation, and γ is the ratio of the mean specific heats $\bar{C}_p/\bar{C}_v$.

The problem is how the molecules in contiguous layers ahead of a detonation wave[1, 2, 3] acquire their activation energy in the very short time available. In the present development of experimental and theoretical work, the kinetics of rearrangement of chemical binding and liberation of chemical energy is sufficiently characterized by the total time required for energy release, i.e. the period Υ elapsing between the first arrival of the head of a detonation wave, at any group of molecules, and the time when the reaction products are essentially in instantaneous thermodynamic equilibrium. Another way of putting it is that the distance $X = D\Upsilon$ gives the depth of the zone behind the detonation front in which the molecules are not in chemical equilibrium and in which irreversible liberation of chemical energy is taking place, where D is the detonation velocity.

Simple consideration shows that the activation processes in this reaction zone must be much more rapid than for ordinary physicochemical reactions. Any layer of molecules, which might have a thickness of about 2×10^{-8} cm, would be traversed by the head of a detonation wave, travelling at 7,000 m/sec in about 3×10^{-14} seconds. During this extremely short time random collisions are not of sufficient frequency to account for the high velocities of energy release which are necessary to maintain the detonation wave, but it should be noted that the streaming velocity is added on to the random molecular velocities arising from the high temperature of the products in the reaction zone. Molecules in the quiescent layer immediately ahead of the detonation wave are activated *a* by the random translational energy of the hot reaction products and *b* by the directed translational energy corresponding to the streaming velocity.

It is very important to determine how fast molecules such as TNT actually decompose under these extreme conditions. Elementary hydrodynamic theory of detonation pays no regard to the mode of energy release which maintains the detonation wave. Essentially, it considers the passage of a shock wave through the explosive, under such conditions that the heat of chemical reaction is fed into the front of the shock wave and serves to maintain its intensity. When this assumption begins to break down because the chemical energy cannot be liberated sufficiently rapidly, the observed detonation velocity will begin to fall below the value calculated on the basis of elementary hydrodynamic theory. Experimental methods of studying the rate of chemical reaction in the detonation wave depend essentially on establishing critical conditions of detonation, such that the observed detonation velocity is sensitive to these conditions.

In gaseous systems, the effects of initial temperature and initial density on the stability of detonation should be of particular value in elucidating the mechanisms of activation. Experimental studies of such effects have not been carried very far and will not be discussed further here[9, 10]. In solid explosives, use has been made of measurements of the critical effect of charge diameter on detonation velocity, *measured for cylindrical charges*[1]. When the detonation wave reaches any given layer of molecules, the chemical reactions initiated begin to release the energy which maintains the detonation, but owing to the fact that it is impossible to have infinitely rigid walls to a cylindrical charge, the high pressures immediately behind the detonation cause the walls to move outwards at a finite rate which can be calculated If the velocity of reaction is sufficiently great, substantially all the energy release will have occurred before such outward movement is appreciable Under these circumstances the experimental detonation velocity is equal to that calculated on the basis of elementary hydrodynamic theory If the reaction velocity is somewhat slower than is required to attain this limit, appreciable outward movement of the walls of the charge takes place before energy release is completed As a result, the average pressure and temperature behind the detonation front are smaller than calculated for the limiting conditions It can be shown that the observed detonation velocity D is smaller than the detonation velocity D_0 at infinite charge radius, in accordance with a relationship of the form

$$(D_0/D)^2 = 1 + f(X/R)$$

where $f(X/R)$ is a function of the ratio of the thickness of the zone for energy release X to the radius R of the charge According to the conditions at the boundary of the charge (bare charge, thin laminar metal walls, very thick metal walls) this function takes various forms, which can be calculated

The experimental results can be illustrated by reference to the detonation of 60/40 TNT-NH_4NO_3 the well known 'amatol'[9] By carrying out measurements on the detonation velocity at various charge diameters and for various boundary conditions, the theoretical equations have been verified Values of Υ have been found to depend in a characteristic way on the size of the ammonium nitrate crystals, which can be varied For example, with a grist size giving a surface area of 195 cm²/gm the observed reaction time for energy release is 3 1 microsec, and with a grist size giving a surface area of 310 cm²/gm the reaction time is 2 1 microsec A general relationship has been found between the *surface area* of the ammonium nitrate A_1 and the reaction time Υ in microsec, of the form for 60/40 TNT-NH_4NO_3

$$\Upsilon = 3\ 7 \times 10^{-4}/A_1 + 9 \times 10^{-7}$$

Analysis of this and other data on reaction velocities in the detonation zone[1] lead to the important conclusion that in detonation the rate controlling processes have small temperature coefficients i e they do not involve 'activation' as ordinarily understood Probably with solid 60/40 TNT-NH_4NO_3 the TNT first reacts in a time of about 10^{-7} sec to give its detonation products at very high temperatures and pressures, and the NH_4NO_3 crystals gradually erode in these hot detonation products, at a rate controlled by their surface area In the detonation zone there is a superabundance of hot molecules of various kinds, and the supply of activation energy is not the limiting factor. Rates of diffusion and volatilisation are of controlling importance, owing to the need for bringing molecules into juxtaposition before the rearrangement of chemical bonds can take place with the release of chemical energy

SUMMARY

The stimulus required to initiate progressive energy release in an explosive determines its 'sensitiveness' Development of fundamental research on the sensitiveness of explosives has extended existing physicochemical theories about activation energy in several ways Three main types of activation process must be considered with reference to the sensitiveness of explosives

1 According to the type of sensitiveness considered and the explosive envisaged, the primary process which 'triggers' energy release may involve thermal or tribochemical activation of the molecules of explosive

2 The growth of a primary 'hot spot' normally involves thermal activation of contiguous molecules Non-thermal activation may however be important, for example in initiators

3 In a detonation wave, activation of successive layers of explosive molecules involves both random and non-random processes of activation

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Experimental Design

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THE development of statistical techniques in recent years has been accompanied by a complementary development of experimental method. The statistician, in analysing experimental data, has also cast light upon the best methods of designing experiments and, in turn, these methods have demanded new statistical tools. Foremost in this development of new techniques and methods, R A FISHER[1] has laid down the fundamentals of modern experimental design and, using Fisher's work as a basis, other authors have extended the range and types of efficient design. This work, originally applied only to agricultural research, has become increasingly used in all branches of science as the advantages of efficient experimental design have been realized, and a wide variety of experiment designs has been derived.

It is impossible here to give a full account of the growth of this subject, but the following sections are intended to indicate the main lines of development.

MAIN CONCEPTS IN EXPERIMENTATION

One of the main purposes of experimentation is the determination or measurement of effects. Although this is not the only purpose, it is the one with which the statistician is most concerned. For example, an experiment may test the effect of a treatment, then it is necessary to determine whether the treatment has an effect, and if so to measure the size of this effect. There are, in fact, two requirements in such an experiment: first, it must give rise to valid estimates of the treatment effect or effects and secondly, it should also allow the accuracy of these estimates to be determined. To elaborate these points, suppose that, in order to test the effect on bone weight of increasing the fluorine content of a normal diet, two groups of rats are fed diets with normal and high levels of fluorine. The comparison of the average bone weights on each diet would be influenced by the proportions of male animals on each diet so that, if possible, we should arrange for these proportions to be equal. Similarly, the weights of the animals may tend to influence the comparison so that we might choose the two groups to be similarly constituted by weight. This relatively simple idea of making the groups as similar as possible and, in the limit, pairing-off the animals in the two groups may be called stratification.

However, even if the two groups are equalized in all known factors, unknown quantities will still cause some disparity, which can seldom be removed. The answer to this difficulty is to ensure that the magnitude of any disparity can be gauged. To achieve this we have to ensure that such disparity is evenly distributed within the framework imposed by the stratification. Thus, for example, suppose we have four 'similar' rats receiving the two diets and that the measurements of those receiving the normal diets are N_1, N_2 and those the diets high in fluorine content are F_1, F_2. The comparison between $N_1 + N_2$ and $F_1 + F_2$ will then indicate the effect of the fluorine, but will also be affected by unaccountable variability. However, the comparisons between $N_1 + F_1$ and $N_2 + F_2$, and between $N_1 + F_2$ and $N_2 + F_1$ are unaffected by any dietary effect and may be used to indicate the magnitude of the unaccountable variability, provided that these comparisons are as likely to be affected by such non-dietary factors as the dietary comparison. For this reason it is necessary to carry out randomization i.e. the allocation of animals at random to the diets within the stratification framework, to allow the accuracy of the comparison to be gauged. Thus, where the animals have been paired, one animal from each pair is allocated at random to each treatment. This randomization is usually carried out with the aid of a 'table of random numbers' to avoid any possible personal bias. Such tables have been compiled by R A FISHER and F YATES[2], who also give an account of the methods of application.

The above example emphasizes certain other necessary features of experimental design. First, in order to be able to estimate the variability to which the treatment comparison is subject, replication is necessary i.e. more than one measurement should be taken for each treatment. Secondly, since the idea of randomization refers to the measurement, it is of no use to randomize the animals and then keep all animals receiving the same diet together, since this would defeat the purpose of randomization. Thirdly, the more stratification is used the less randomization is possible and, correspondingly, the accuracy of the comparisons cannot be so well determined. This last point is particularly interesting. It indicates that a balance must be struck between the one extreme in which the effects are inaccurately determined, but we know with some precision their accuracy, and the other extreme in which the effects are accurately determined, but we do not know how accurately. We wish, in fact, to estimate both the effects and their accuracy if we are to verify their existence, and we shall wish to choose the most sensitive or efficient experiment.

TYPES OF EXPERIMENTAL DESIGN

Experiments may be classified, broadly speaking, into two main groups experiments carried on through several phases, such as crop-rotation experiments and experiments involving growth curves, and experiments with a single phase These two types are usually called long term and short term experiments but whereas a short term experiment may run for several years *e.g* in agriculture and animal nutrition, some long term experiments will be completed in a few hours

Each of these two main types may be further subdivided according to whether it is desired to test one or several sets of factors simultaneously and, for the long term experiment, according to whether the factors to be tested remain constant throughout all phases of the experiment or vary in different phases The appropriate experimental designs for each of these types will now be considered

Short term experiments to test a single set of factors— The simplest type of design for this purpose stratifies each replication and randomizes the treatments within the replication This design is known as randomized blocks For example, if we wish to test five treatments, *A, B, C, D, E*, the design may be

E, D, A, C, B , *A, C, E, B, D* , *B, E, C, D, A* , *etc*

These ' blocks ' may be spatial, temporal or may refer to the material used The number of replications or blocks that are used will depend both upon the variability in the measurement and upon the accuracy that is desired As a rough guide, if n replications are used and the unaccountable variability in each measurement is about p per cent then an experiment of this type should be able to detect a difference of about $p\sqrt{(8/n)}$ per cent

If the number of replications is equal to the number of treatments, then we may stratify with respect to two factors simultaneously An example of such a design is

E	*D*	*A*	*C*	*B*
A	*E*	*C*	*B*	*D*
C	*B*	*E*	*D*	*A*
B	*C*	*D*	*A*	*E*
D	*A*	*B*	*E*	*C*

Each treatment occurs once in each row and once in each column in this design, so that it is possible to eliminate the row and column effects in comparing treatments This design is known as a Latin square Commonly, designs of this type are considered as eliminating spatial effects *e g* in agricultural field trials, but they may eliminate temporal effects *e g* columns representing successive days and rows representing time of day, or a mixture of spatial and temporal effects A considerable improvement in accuracy may result from the elimination of row and column variation but, as pointed out above, the amount of stratification that can be carried out is limited by the necessary determination of the accuracy of the treatment effect This makes the Latin square design unsuitable for testing less than five treatments unless several Latin squares are used simultaneously Fisher and Yates' *Statistical Tables* gives Latin squares to test up to twelve treatments and also describes how these should be randomized

When the number of factors is large, then the Latin square design becomes unwieldy and even the size of a randomized block design may become too large (especially if the block is a unit of time) For this reason, experiments have been planned in which the strata or blocks do not contain a complete replication, but in which there is still a balance between the factors involved Two main designs of this type may be mentioned balanced incomplete blocks and lattice squares A typical example of a balanced incomplete block design is

E, C, G, A , *F, E, D, C* , *D, G, E, B* ,
C, G, B, F , *C, B, A, D* , *G, D, A, F* , *E, A, F, B*

In this design there are four replications of seven treatments arranged in seven blocks so that each pair of treatments occurs together twice Designs of this type are particularly useful where it is known that the variation within each block is small compared with the variation between blocks *e g* where each block represents animals from the same litter, material from the same batch or measurements taken on the same day Fisher and Yates also give a list of the most suitable designs of this type

The lattice square designs are arranged so that row and column effects can be eliminated but here it is the result of a balanced arrangement of treatments in rows and columns The number of treatments must be a perfect square but it is possible to repeat some of the treatments to make up the necessary number The replications are then arranged so that every pair of treatments occurs together either in the same row or column An example of this type of experiment is provided by the following design for twenty five treatments

Block *1*	*S*	*Y*	*G*	*M*	*A*
	K	*Q*	*D*	*J*	*W*
	E	*F*	*R*	*X*	*L*
	V	*C*	*O*	*P*	*I*
	H	*N*	*U*	*B*	*T*
Block *2*	*W*	*N*	*G*	*P*	*E*
	S	*J*	*C*	*L*	*U*
	F	*V*	*T*	*D*	*M*
	B	*R*	*K*	*Y*	*I*
	O	*A*	*X*	*H*	*Q*

Block *3*

G F I H J
V U X W Y
L K N M O
B A D C E
Q P S R T

F YATES[3, 4] has given an account of this and associated designs

Short term experiments to test several sets of factors— It is frequently necessary to carry out experiments to test several sets of factors simultaneously The classic example is the fertilizer experiment where different fertilizers have to be tested on different variates possibly under different conditions of cultivation, but similar experiments to test, say, methods of processing different materials or treatments applied at different times are fairly common A possible design for such an experiment is the Graeco-Latin square

$D\delta$ $C\varepsilon$ $E\alpha$ $A\gamma$ $B\beta$
$B\alpha$ $A\delta$ $C\gamma$ $D\beta$ $E\varepsilon$
$A\varepsilon$ $E\beta$ $B\delta$ $C\alpha$ $D\gamma$
$C\beta$ $B\gamma$ $D\varepsilon$ $E\delta$ $A\alpha$
$E\gamma$ $D\alpha$ $A\beta$ $B\varepsilon$ $C\delta$

In this design the Greek letters represent one set of treatments and the Latin letters represent a second set Each Latin letter occurs once with each Greek letter and they both occur once in each row and once in each column so that row and column effects can be eliminated However, designs of this type are usually limited in application since it is only possible to compare the average effects of each set of factors For example, if we were testing the resistance of mice bred on different diets to different strains of bacteria, we should be able to compare the resistance on different diets averaged over all strains and *vice versa*, but we cannot test whether the best diet is uniformly the best against all strains of bacteria Frequently it is necessary to test not only the effects but also their uniformity under the range of conditions tested and for this purpose it is necessary to use the factorial design This employs every possible combination of the sets of factors and permits the consistency of the effects to be examined As an elementary example of such a design, consider the following which tests the combinations of four treatments A, B, C, D

Control, A, B, AB, C, AC, BC, ABC,
D, AD, BD, ABD, CD, ACD, BCD, $ABCD$

where these sixteen treatment combinations are randomized and replicated before application A more complicated example is provided if we wish to test and compare, say, two treatments A_1 and A_2, and three treatments D_1, D_2, D_3, as well as B and C The design, then becomes

Control, A_1, A_2, B, A_1B, A_2B, C, A_1C, A_2C, BC, A_1BC, A_2BC
D_1, A_1D_1, A_2D_1, BD_1, A_1BD_1, A_2BD_1, CD_1, A_1CD_1, A_2CD_1, BCD_1, A_1BCD_1, A_2BCD_1
D_2, A_1D_2, A_2D_2, BD_2, A_1BD_2, A_2BD_2, CD_2, A_1CD_2, A_2CD_2, BCD_2, A_1BCD_2, A_2BCD_2
D_3, A_1D_3, A_2D_3, BD_3, A_1BD_3, A_2BD_3, CD_3, A_1CD_3, A_2CD_3, BCD_3, A_1BCD_3, A_2BCD_3

This gives forty eight treatment combinations.

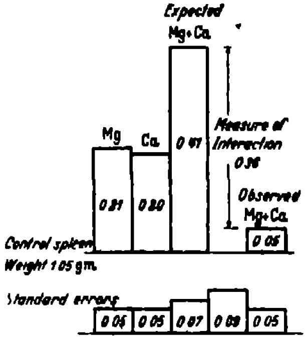

Figure 1 *Interaction in a mineral metabolism experiment*

If, in the application of a factorial design, the effect of one factor changes when a second factor is applied, then the two factors are said to interact Such interactions are often as important as the average effects *Figure 1* gives an example of interaction in a mineral metabolism experiment While supplementary calcium and magnesium both lead to an increase in the spleen size of male rats, when they are simultaneously given, the expected increase from their joint application is not realized When calcium and magnesium are both given, the difference between the expected and observed increases indicates the existence of interaction Since each of these values is subject to error, the 'standard error' of each value is indicated at the bottom of the diagram

In this manner, factorial design permits the investigation of the optimum combination of treatments and the manner in which the treatments jointly behave However, in practice, certain modifications of the ordinary factorial design are desirable

First, some form of stratification might be adopted to allow the effects and principal interactions to be determined, using fairly uniform material Thus, if the sixteen treatment combinations of the former factorial design are arranged in two blocks of eight treatments, we get

Block *1*

Control, AD, BD, AB, CD, AC, BC, $ABCD$,

Block *2*

D, A, B, ABD, C, ACD, BCD, ABC

Then each treatment and each pair of treatments occurs equally frequently in each block By this device, known as confounding, the main comparisons are made within the blocks F YATES[4, 5] has given accounts of the factorial experiment and the principles of confounding M M BARNARD[6] has enumerated the possible confounding arrangements when each of the factors is at two levels, while O KEMPTHORNE[7] has indicated a mathematical approach to confounding

Secondly, if the number of sets of factors to be tested is large, then the number of observations may be very large especially if the treatment combinations are replicated Fortunately, however, in this instance, F YATES[8] has shown that it is usually possible to estimate the unaccountable variation without replication This fact makes the factorial design very useful for testing large numbers of factors simultaneously

Further developments in short term experimentation—The designs given in the last two sections are the most commonly used However, alternative designs may be used for particular purposes Thus, for example, if particular comparisons are of greater importance, then the accuracy of these comparisons may be improved at the expense of the other comparisons This is done by stratifying with respect to the more important comparisons, but not for the others As an example, suppose in a factorial experiment to test A, B, C and D, the effect of D is more important than those of A, B and C The design might then be arranged so that neighbouring observations were both with and without D Thus the randomized design might be

C, CD, ACD, AC; B, BD, ABC, $ABCD$,
BC, BCD, ABD, AB, AD, A, *Control*, D

This type of design is usually called a split-plot design D. J FINNEY[9] and O KEMPTHORNE[10] have recently given accounts of the application of the split-plot method

In industrial experiments it is sometimes possible to assume that certain factors or treatments will act independently Then an alternative to the factorial design can be devised to test the main effects only For example, if we wish to test five treatments, A, B, C, D, E, the treatment combinations

A, B, C, D, E, ABC, ABD, ABE, ACD, ACE,
ADE, BCD, BCE, BDE, CDE, $ABCDE$

may be used The effect of each treatment can be measured by comparing the set of eight observations which contain this treatment with those that do not Replication is unnecessary here R L PLACKETT and J P BURMAN[11], C R RAO[12], and D J FINNEY[13] have all dealt with particular aspects of such designs

Long term experiments—The principles governing the long term experiments are similar to those for short term experimentation. Where observations taken in successive phases of the experiment are independent and where there is no 'carry over' effect of the treatments, the experiment may often be planned in the same manner as a short term experiment with the phases regarded as an extra set of factors to be eliminated and tested Thus, the rows or columns of a Latin square may be taken as successive phases of an experiment, and corresponding designs may be used for factorial experiments For example, three independent treatments, A, B, C, may be tested using a design

Position	*Phase* 1	2	3	4
1	*Control*	BC	ABC	A
2	C	B	AC	AB
3	AB	AC	*Control*	BC
4	ABC	A	B	C

In general, the major difficulty is in the analysis of such experiments, unless it is possible to predict the manner in which the mean and unaccountable variability change from phase to phase The same difficulty attaches to experiments with carry over effects, but the need for estimating and eliminating these leads to further experimental designs If the factors or treatments remain constant throughout the experiment the designs for short term experiments may be used, but if the factors rotate then alternative designs must be employed

Long term experiments with rotating factors may be designed either for the purpose of estimating the residual effects of treatments or to increase the accuracy of treatment comparisons For example, in agriculture, a rotating-factor experiment may compare the effects of different crop or treatment rotations, or it may rotate the treatments on particular areas or on certain animals, so that comparisons between treatments are made on the same area or animal The simplest design for this experiment employs the treatment sequences A, B, A, B, A and B, A, B, A, B In this design only the latter purpose of comparing treatments on the same area or animal is served, since it is impossible to separate the effect of B from the residual effect of A, and *vice versa*

If it is desired to measure residual effects, then it is always necessary to make certain assumptions concerning the manner in which they act Normally, it is assumed that after a certain time the residual effects are constant or zero, and that they are not influenced by the ensuing treatments With these assumptions, it is possible to estimate residual effects with experiments such as

Position	*Phase* 1	2	3	4	5
1	A	B	C	A	B
2	B	C	A	B	C
3	C	A	B	C	A
4	A	C	B	A	C
5	B	A	C	B	A
6	C	B	A	C	B

where the rotation repeats itself after three phases, and each treatment is applied twice in each phase and followed by the other two treatments W G COCHRAN[14] has given an account of experiments of this type and more complicated designs However, it is particularly true of long term experiments that the design is determined by the behaviour of the treatments This results in a wide variety of designs for particular purposes which are still under investigation and cannot be dealt with briefly

ADVANTAGES OF PLANNED EXPERIMENTS

The main advantage of planned experiments is that valid estimates of treatment effects are obtained the accuracies of which are determined simultaneously Thus, while in the unplanned, uncontrolled experiment we may possibly be misled concerning the reality of the observed effects, in the planned experiment we are able to specify the odds against an observed effect being due to chance variation A second point is that the planned experiment will frequently lead to more accurate estimates of treatment effects and consequently to an appreciable saving in labour Thus, for example, F YATES[8] showed that two particular experiments using Lattice squares were 30–60 per cent more accurate than corresponding experiments employing randomized blocks Many other examples of such improvements could also be quoted It should not, in consequence, be assumed that the complex design should always be used in preference to the simple but less efficient design The results from the complex design may frequently be verified and extended by a series of simple experiments carried out at different times and under different conditions This is particularly true in agriculture, where the findings from the complex field experiment may be tested in a series of simple experiments in cultivators' fields

A further advantage in favour of the planned experiment is that the determination of the accuracy of its comparisons frequently allows the experimentation to be extended if necessary Consequently, the results of any particular investigation can be accurately supplemented by further experimentation. However, in considering the advantages of planned experiments, it should be remembered that these might be nullified if the wrong design is used or if unforeseen difficulties occur For these reasons, the cooperation and advice of a statistician are to be recommended in the designing of experiments

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Artificial Lactation and Perfusion of the Bovine Mammary Gland

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BY artificial lactation we do not mean in this instance the induction of lactation in virgin goats or maiden heifers by implantation of synthetic oestrogens, but the lactation which is obtained when a bovine mammary gland is excised and perfused Such a technique was described by W E PETERSEN, J. C SHAW and M. B. VISSCHER[1] When we ourselves began work along these lines[2] we were quite unaware of this technique of Petersen, because of war conditions As might be expected there are a number of similarities between Petersen's technique and our own, but there is also a fundamental difference Whereas Petersen uses the bovine mammary gland in the intact state, we divide it symmetrically into two portions by cutting the connective tissue septum down the median line without damaging the glandular tissue A single udder thus provides two halves which, from the physiological point of view, can be regarded as two perfectly analogous organs

These two halves are perfused separately, our perfusion apparatus comprising a double installation The great advantage of this technique is that there is no mixing of the blood traversing the two halves Complete separation of the two halves is necessary for comparison of the function of the one with the other If the two halves are perfused each by means of its own separate apparatus there is nevertheless considerable admixture of blood between the two systems, on account of the numerous venous anastomoses, unless a complete anatomical separation is made

It is evident that our technique has several advantages, the main one being that one udder-half serves as a control for the other, which can be subjected to various experimental conditions at will This means that the number of experiments, always exacting, necessary to enable definite conclusions to be reached is minimized

The disadvantage of our technique is that it prolongs, to a certain extent, the manipulation of the udder which must be carried out before the perfusion can be started This drawback does not seem to be serious, however, since in all our experiments both udder-halves respired and lactated perfectly

APPARATUS AND TECHNIQUE

In describing the apparatus we shall refer only to the perfusion of one half of the udder since the apparatus is completely symmetrical Only the thermostat gear and the respiration pump are common to both perfusion systems

From the reservoir *A* the blood is brought to the artificial heart *B* For this purpose the air pump *D* and the special valves *c* and *c'* are used The blood is then driven to a thermostat *a'*, in which it circulates slowly and attains a temperature of 38°C It is then conducted to the corresponding udder-half The venous blood issuing from this udder-half is collected in a rubber drain *I* and reaches the artificial lung *K*, where it is oxygenized, and returns to *A* By means of a special valve *O* the blood pressure is automatically regulated and kept constant at 120 mm Hg

Figure 1a also represents the mode of suspending the gland *Figure 1b* shows the special device *E* constructed to slow down the circulation of the blood in the thermostat *a'* so as to warm it up to the experimental temperature For more technical details the original publication[1] should be consulted It should however be emphasized here that thorough filtration of the blood is indispensable

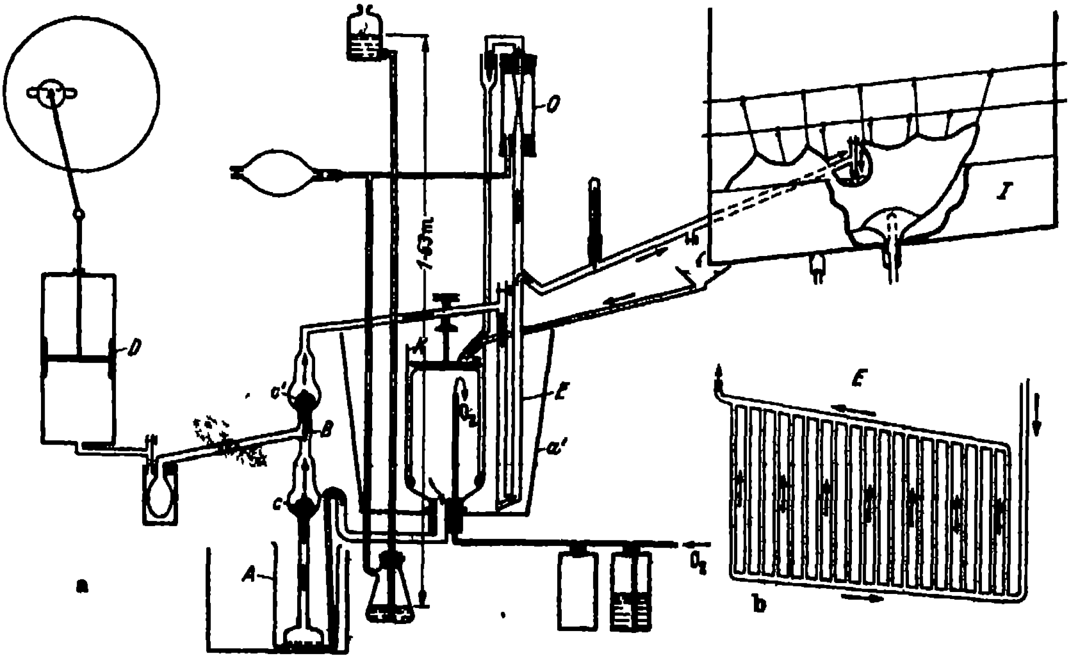

Figure 1 a diagram of apparatus for perfusion of udder b special device for slowing down circulation of blood in thermostat

Soon after the start of the experiment 5 to 10 i.u. pituitrin is injected into the artery of each udder-half: this causes an immediate ejection of milk. The first 300 ml of venous blood following the injection is discarded in order to avoid vaso-constriction effects during the experiments. To collect the milk formed during the experiment glass canulae are introduced in the galactophorous sinuses, after which the teat sphinctures are amputated. At the end of the experiment an injection of pituitrin ensures the complete ejection of milk.

Our perfusions have never been carried on for longer than two hours so as to avoid the risk of bacterial contamination.

Usually the blood of the animal providing the udder is used. The blood is obtained by opening the carotid and jugular after the animal has been shot. It is collected in paraffined iron vessels. Coagulation is prevented by addition of heparin. The choice of the anti-coagulant is very important as is explained below.

IMPORTANCE OF ANTI-COAGULANT AND NECESSITY FOR CALCIUM IONS

The question of the anti-coagulant[3] has been specially studied since heparin is very expensive. We have tried to replace heparin by calcium citrate.

In this series of experiments we perfused one half of the gland with heparinized blood and the other with citrated blood. Since the anti-coagulant action of citrate is based on the elimination of Ca^{2+}, citrated blood must be considered as a fluid poor in Ca^{2+} while heparinized blood is normal from this point of view. Before perfusing with blood the milk which had accumulated in the galactophorous sinuses, and which must not be included in the experiment, was removed. As soon as the perfusion began the milk flowing from the teat cannulae was collected; when this rapid flow ceased 10 i.u. of unfractionated posterior-pituitary extract was injected into the artery with the object of completely emptying the two udder-halves of their contained milk. The perfusion was continued for two hours; at the end of it the gland was emptied by another injection of unfractionated posterior-pituitary extract.

Results were as follows:

1 as soon as blood begins to flow through the udder-halves there is a flow of milk but only from the half perfused with heparinized blood.

2 when this rapid initial milk flow has ceased and an injection of 10 i.u. of unfractionated posterior-pituitary extract made into each artery, the udder-half perfused with heparinized blood exhibits a pronounced vasoconstriction resulting in a marked diminution of blood flow. The udder-half perfused with citrated blood exhibits little or no vaso-constriction. We have measured the venous output from both udder-halves and found the value for the citrated side to be double that from the heparinized side (260 ml/min as against 130 ml/min with essentially the same values on repeating the experiment).

3 at the end of the experiment, i.e. after perfusion for 2 hr we have collected, following another injection of 10 i.u. unfractionated posterior-pituitary extract to empty the glands, less milk from the citrated side (60 ml) than from the heparinized side (90 ml). If at this time we switch the two circulations so that the udder-half previously perfused with the heparinized blood is now perfused with the citrated blood and *vice versa* there is a flow of milk from the heparinized half but none from the citrated half. In other words, we may conclude that the pituitary hormone does not exert an optimal effect on the udder-half perfused with citrated blood, which however can be emptied as soon as it is perfused with heparinized blood.

These observations demonstrate the importance of calcium ions. Since there is no initial milk flow from the citrated side we can conclude that the hormone causing milk expulsion (the existence of such a hormone will be discussed later) has no action on the contractile elements in the absence of insufficient concentrations of Ca^{2+}. Since the vaso-constriction occurs only in the udder-half perfused with heparinized blood we may conclude that vasopressin does not exert its effect when the concentration of Ca^{2+} is sub-optimal.

Unfractionated posterior-lobe extract caused only a partial ejection of milk from the citrated udder-half. It follows that in the absence of a sufficient concentration of Ca^{2+} the posterior-pituitary hormone is unable to cause complete contraction of the contractile elements of the gland just as we have found (and pointed out above) in the case of the hormone causing milk expulsion.

MILK EJECTION IN CATTLE, THE EJECTION HORMONE

The researches of F. ELY and W. E. PETERSEN[3] show that in the cow the expulsion of milk is not under the direct control of the central nervous system. These authors have shown that section of the nerve fibres innervating one half of the udder does not affect the expulsion of milk. On the other hand injection of pituitrin causes a more complete emptying of the udder than occurs with normal milking[4].

Ely and Petersen have postulated that a great number of exterior stimuli normally associated with milking, such as manipulation of the teats, the rattle of milk buckets *etc* stimulate, through the central nervous system, the secretion by the hypophyseal posterior lobe of the oxytocic hormone into the blood Oxytocin causes contraction of the contractile cells present in the udder and is thus the immediate cause of the ejection of milk According to Ely and Petersen we are here dealing with a conditioned reflex

W E PETERSEN and T M LUDWICK[6], working with the excised bovine udder, perfused and emptied as completely as possible by milking, have shown that if a whole udder is perfused with blood from a normal cow there is no ejection of milk If, however, the udder is perfused with blood from a cow which has been subjected to the milking stimulus, an ejection of milk is observed This blood must therefore contain a chemical substance which evokes milk ejection, a substance which appears to be destroyed if the blood is kept at room temperature for half an hour

These observations of Petersen are so important that, in our opinion, they justified our carrying out a quantitative research on this question Our perfusion method is well suited for this purpose For experimental animals we have used cows giving 5 to 6 l of milk daily In each case the udder was free from mastitis, acute or chronic, and the two udder-halves were absolutely symmetrical and identical from the gross anatomical and physiological viewpoints

Before killing the animal we took 4 l of blood from the jugular vein, using the largest possible trocar and cannula so as to cut down the blood sampling time The blood was collected in a conical flask containing 250 mg heparin

The udder was at once washed with hot, soapy water, a procedure which caused the cow to 'let down' her milk into the udder cisterns so that the teats became turgid Moreover, the teats were manipulated for 2 to 3 min without milking the animal

The animal was then killed and a further 4 l of blood collected in a conical flask containing 250 mg heparin The udder was excised and perfused with physiological saline to wash out all blood from the vessels It was then dissected down the midline and two absolutely symmetrical udder-halves obtained On inserting cannulas into the teats a considerable quantity of milk was drawn off This milk was present in the udder cisterns and larger ducts because of the manipulation, referred to above, to which the udder and teats were subjected As soon as the flow of milk ceased, perfusion of the two separate udder-halves was begun.

We perfused the left udder-half with the blood collected before the above mentioned manipulation of the udder and teats, the right half being perfused with blood collected after these manipulations Immediately after the beginning of the perfusion a fresh flow of milk from the teat cannulae was observed Milk from the right and left udder-halves was collected separately We should like to draw particular attention to the fact that the two halves were absolutely separate and the possibility of admixture of the blood from the two halves was completely excluded

This experiment has been repeated four times with the results given in *Table I*

Table I

Experiment number	*Left udder-half milk yield ml*	*Right udder-half milk yield ml*
1	160	360
2	270	520
3	215	345
4	390	500

The milk so collected was evidently present in the ducts before the experiment and was ejected as a result of the perfusion There was some inevitable delay between the slaughter of the cow and the beginning of the perfusion of the isolated udder In the first two experiments this amounted to about 60 min and in the last two about 80 min

These results clearly indicate that more milk was in each example ejected from the right udder-half *i e* from the half perfused with blood drawn after stimulation of the udder and teats This agrees with the results of Petersen and Ludwick and shows that after stimulation of the udder there appears in the blood a factor causing expulsion of milk

Nevertheless there was, at the same time, an ejection of some milk from the left udder-half *i e* from the half perfused with blood drawn before the udder was stimulated This was to be expected since perfusion causes an increase in the volume of this udder-half and in consequence the galactophorous canals and sinuses are subjected to increased pressure resulting in expulsion of milk

In experiments *1* and *2* perfusion began 60 min after the cow was slaughtered The differences between the quantities of milk collected from the two halves is here considerable The factor which appears in the blood after manipulation of the teats was therefore thus still detectable after 60 min.

The differences are smaller in experiments 3 and 4 in which the blood remained 80 min at environmental temperature before the perfusion began. The blood gradually lost its activity during this time. According to Petersen the activity is destroyed after 30 min, while we have observed marked activity after 80 min.

Our experiments show that after stimulation and manipulation of the teats a factor which evokes expulsion of milk appears in the blood, however they do not give any indication of the site of formation of this factor.

PHYSIOLOGY OF THE CISTERN

The perfusion technique enables the physiology of the cistern[7] to be studied. The cistern pressure is determined as shown in *Figure 2*. As indicated in this figure the base of one teat is cut and a metal cannula (6 mm diam) is inserted into the cistern. One of the arms of the cannula is connected to a manometer filled with milk, one limb of which is open and the other connected to a Marey tambour which registers changes of pressure in the cistern.

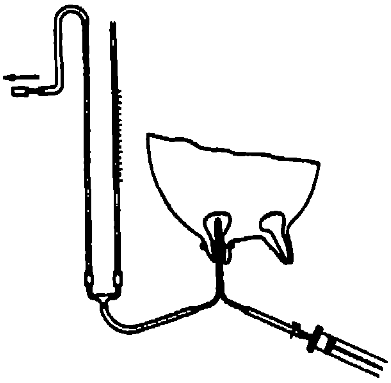

Figure 2 Registration of cistern pressure

The principal findings may be summarized as follows:

a if one fills the cistern rapidly the pressure record shows a typical inflection when the pressure attains 20 cm Hg. This inflection is probably due to the opening of valves in the canals of the udder.

b as soon as the cistern is full the pressure diminishes rapidly because of relaxation of the cistern wall and because of the passage of milk into the deeper ducts. In one case the cistern showed feeble rhythmic contractions.

c if the cistern is filled by successive fractions amounting to 200 ml, the increase in pressure is slow and regular. The pressure records obtained with the isolated organ and in the living animal are similar.

d the filling of the cisterns causes an increase in the blood pressure in the large veins near the base of the teat.

e pitocin causes a flow of milk from the alveoli into the cistern and an increase in the cistern pressure.

f adrenalin diminishes considerably the cistern pressure because it causes vasoconstriction.

g if an isolated udder is perfused with blood from a freshly milked cow the cistern pressure increases to the same extent as after the injection of pitocin.

h neither smooth muscle nor sympathetic nerve fibres exert any important influence on the physiology of the cistern.

BIOCHEMICAL ASPECTS

Our perfusion method is useful for a variety of physiological experiments. Thus it has enabled us to study the innervation of the mammary gland[8] but has not proved satisfactory for biochemical experiments for a very simple reason. Because the quantity of blood in the system must be limited on account of the fact that the anti-coagulant is very expensive, metabolites tend to accumulate, thus giving misleading results and obscuring biochemical interpretation. In order to obviate these difficulties we are carrying out perfusions of the sheep udder and we hope, by the use of isotopes, to be able to clarify, at least partially, the biochemistry of lactation.

It is our very agreeable duty to express our thanks here to the Belgian Foundation, I R S I A, which has generously supported our researches and to Dr S. J Foley for translating this article

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Rowett Research Institute

D P CUTHBERTSON, M D, D Sc
Director

It is only within the last ten years that progress has enabled us to investigate problems of nutrition with some degree of confidence, for only recently has knowledge of amino acids, vitamins and trace elements reached a stage which permitted the design of experiments to determine requirements in relation to production But previous experience warns us that our present ignorance will be measured in the future Although we could plan with confidence during the war years we still did not know the answers It was with this in mind that at the end of the war a new attack on the fundamentals of animal nutrition was planned at the Rowett Research Institute

The first task was to create an organization which could make a first rate contribution, and for this scientists capable of making an intimate investigation into the physiological, biochemical and microbiological processes involved in digestion, absorption, metabolism, growth, fattening and reproduction were necessary It was also necessary to see that we had the technical and farm staff, and equipment for the purpose It was early appreciated that the relationship of nutritional state to resistance to disease should be a subject of intensive study, as also host-parasite relationships It was also recognized that problems of nutrition would arise, which although emanating from the practical side would be concerned with the very bases of our knowledge of nutrition

For the tasks in hand the physical equipment of the Rowett Research Institute is being expanded The laboratory block, the original Rowett Research Institute, is now being enlarged by the addition of a third storey and the large and small animal buildings, the latter air conditioned, are also being enlarged. The Reid Library embodies the administrative headquarters, the library proper, and the Commonwealth Bureau of Animal Nutrition In the Duthie-Craibstone Farm of about 900 acres are pooled the joint resources of the Institute and the North of Scotland College of Agriculture

MICROBIAL METABOLISM AND NUTRITION

For many years now the digestibility and nutritive value of potential foodstuffs have been a subject of study at this Institute This work is being extended to determine the influence of pregnancy and lactation on digestibility and the interactions of the protein, carbohydrate, fat, vitamin and mineral components of the diet on the digestibility of the whole ration But, in addition to this traditional line, a more dynamic approach is being developed by the biochemists and physiologists with particular emphasis on the biosynthetic activities in the alimentary tract and what these mean to the organism and in the planning of rations On the mineral side chief emphasis is on the metabolism of bone and the physiological factors which influence it Studies on vitamins and endocrine activities are being initiated

Digestion—effect of micro-organisms— Comparative studies of the nitrogenous and non-nitrogenous compounds in feeding stuffs and ruminal micro-organisms are being conducted with the primary object of finding chemical differences between feeding stuffs and rumen micro-organisms which will permit a means of measuring the development and contribution of the latter to the total ingesta Consideration of the unexpected differences which have been obtained on administering a casein supplement to sheep on a low plane of nutrition by rumen and by duodenal fistula, when placed alongside the observations of others, suggests that microbial deamination may be very rapid with such a protein and may adversely affect its utilization Investigations of the 'non-protein nitrogen' of fodder materials have established that a high proportion of this is represented by α-amino acids in 'free' and 'bound' form In all this work the Van Slyke ninhydrin-CO_2 technique, partition chromatography and electric transport methods have proved invaluable

Observations have also shown that a large proportion of the nitrogen of the rumen contents is situated in the bodies of the micro-organisms and only a small proportion is in the form of soluble nitrogenous constituents Coarse plant residues account for about 30 to 40 per cent of the total rumen content of nitrogen In collaboration with the Macaulay Institute, it has been shown that these micro-organisms concentrate trace elements in their substance This is of particular interest in relation to cobalt and its role in the ruminant Experiments to prove whether or not the action of cobalt is localized in the rumen of the sheep are under way and should soon be completed

Work upon the nuclear material of the rumen micro-organisms of sheep and on the fermentation of pentoses in the rumen and the polysaccharides stored in the protozoa has commenced, also studies on the production of certain members of the B group of vitamins It has been noted that there is a considerable increase in the storage of substances containing glucose in ruminal sediments two to three hours after feeding, but only a small corresponding increase in these substances in the micro-organisms passing out of the abomasum (the fourth stomach in ruminant mammals) The application of quantitative paper partition chromatography to an assessment of substances containing glucose in the micro-organisms of the rumen and abomasum of sheep fed on hay has shown that glucose so combined passes out of the abomasum at the rate of five to six gm per twenty four hours The role of microbial cellulase and glucuronidase is also being studied

Work is designed to characterize on morphological grounds the micro-organisms of the stomach and intestine of sheep so far as this is possible Preliminary work to investigate the mode of the transmission of the protozoa of the rumen has been started

The physiologists are also concerned in studying the flow of food from the abomasum, the rate of secretion and the acidity of gastric juice, the absorption of short chain fatty acids from the rumen and the relative proportions of glucose to fatty acid in the portal blood of sheep

Observations on the physical size of the food particles fed have shown that when immature sheep are fed for a considerable period of time the differing physical character and volume of their digestive organs, rumen in particular, bear a relationship to the bulk of food consumed

Preliminary experiments on the horse and rat have shown that when the animal is forced to eat a diet with a constantly high proportion of dried bracken a conditioned vitamin B_1 deficiency is set up The experimental evidence so far obtained at this Institute indicates that the effect of bracken may be more uncertain in the case of the ruminant Investigations on the ' toxicity ' of red and white clover juices are also being made

While there is thus an integrated study of the role of the microbial population of the rumen this is not the only focus of interest for the microbiologist, for in the large intestine the microbial population plays an interesting role For example, it has been found that uncooked potato starch differs from uncooked maize starch in the pig, in that the maize starch is largely digested in the upper part of the small intestine and absorbed there On the other hand uncooked potato starch largely escapes digestion in the small intestine and reaching the caecum acts as a substrate for micro-organisms The dominant organism in our studies has been a *Clostridium butyricum* which has an α-amylase of considerable interest to our collaborators in the Organic Chemistry Department at Bangor University This organism also produces several vitamins of the B group which make good a deficiency of these in the diet It is presumed that these vitamins are absorbed It would appear that this biosynthetic advantage may be achieved at a lowered economy of carbohydrate There may be an advantage in some of the carbohydrate resisting digestion higher up and acting in the lower bowel as a substrate for the synthesis of B vitamins

The remaining studies on vitamin requirements are mainly concerned with the nutrition of chicks The value of different fractions of liver extracts as sources of unknown factors in synthetic diets and the importance of the level of dietary manganese and choline on bone development are being investigated The possible use of condensed fish solubles (from herrings) as a supplement to all-vegetable rations and the use of herring alkali reduction meal as a partial or complete replacement for white fish meal are being investigated

Mineral metabolism and nutrition—On the mineral side, apart from the work on cobalt already mentioned, an investigation on the depletion and subsequent repletion of calcium in the various parts of the skeleton and the factors involved have been studied at different levels of calcium intake during successive gestations and lactations in the rat The pattern of the investigation is being extended to sheep, and it is hoped to assess the adequacy of grazings by observations on skeletal structure by using chemical histological and x-ray measurements The availability of calcium from various parts of the skeleton during the depletion period and their capacity for subsequent recovery over the repeated pregnancy lactation cycles is also being followed Using a technique involving infiltration of the bone vascular system, the site and degree of mineral depletion can be demonstrated

The response of the skeleton to oestrone and progesterone is being investigated in the calcium depleted animal and studies on the interactions of calcium, magnesium and fluorine, and sex are being made on rats on diets of normal iodine content

Investigations are afoot to determine the pattern of grazing and general feeding behaviour of farm and laboratory animals in relation to physiological state Space permits reference to only one experiment In this it was found that rats allowed the choice of a vitamin B deficient refective or a non-refective diet demonstrated that under these circumstances appetite did not guide the animals to choose the food allowing of survival

Nutrition in relation to infection and infestation—The work of the Pathology Department is mainly concerned with an attempt to define nutritional state in relation to resistance to disease In the first instance attention is being paid to nutrition in relation to resistance to infection So far it has not been possible to isolate the nutritional effect and compare it with other factors known to influence the course of infection—such factors, for instance, as heredity, dose of infecting agent, previous contact with the infection, environmental temperature, ventilation and hygiene The principle adopted by the Institute is to use small animals to establish as many unequivocal relationships as possible then to define the dietary factors responsible for their mode of action and finally to see whether we have discovered anything which can improve the advice we have to offer on the feeding of domestic animals and man It has been found that mice reared and maintained on the Rowett Institute stock diet exhibited a greater degree of resistance to the spread of tuberculosis than did a comparable group on the Sherman-B diet although both diets supported good breeding performances These two diets did not differ in the resistance they conferred against salmonella infection This distinct difference in resistance to tuberculosis is one of the first examples of an effect on resistance to infection brought about by nutritional state So far it has not been possible to find the factor or factors responsible for this difference The use of chicks as an experimental animal for studies on infection is also being explored The influence of a conditioned pyridoxin deficiency produced by excess of vitamin B_1 in the diet, on the growth, reproduction and health of rats is being followed, as is also a glomerular lesion which has been observed in the kidneys of rats fed on a pyridoxin deficient diet

It has been found that a dietary supplement rich in protein led to an increased antibody formation in Blackface ewes immunized against diphtheria toxoid with a resulting higher level of passive immunity in the lambs The same dietary supplement had a favourable influence on the worm burden as judged by weekly faecal egg counts of Blackface lambs but not of the ewes themselves

Collaborative work has begun on the cause and prevention of proliferative dermatitis ('Strawberry footrot') of the legs in sheep

In commercial piggeries which are generally cold and damp there is a high death rate amongst the young animals—particularly after the third week of life and often about the fifth or sixth week At one stage it was thought that the primary factor was an iron deficiency, but although iron does in part improve the haemoglobin concentration, experience has shown that this is not the primary factor Research at this Institute suggests that excessive cooling may be responsible for the lesions observed in the livers of the young animals that die near the time of weaning To investigate the matter further a team to make psychoenergetic studies on pigs is being established

EFFECT OF PLANE OF METABOLISM AND NUTRITION

An experiment to determine the long term effect on health and normal production span of feeding iodinated casein to dairy cows during successive lactations is still being continued Treatment given for 16 weeks during the declining phases of lactation appears to be effective in increasing the yield for about six weeks only It seems to have an adverse effect on the length of lactation and subsequently on the total yield

The remainder of the experiments to be described are concerned with planes of nutrition One of these is an experiment with identical twins planned to determine the effect of different planes of nutrition on growth, yield and the health of dairy cattle The main purpose behind the experiment is to determine if the character of the diet in early life has an influence on the development of the alimentary canal, the rumen in particular, so that it permits a greater intake during the first and subsequent lactations

It has been found that ewes which had been stunted during their first pregnancy in adolescence have after two to three years on a good nutritional plane still not reached the weights or skeletal sizes of those on a good nutritional plane throughout There is some indication that development of the sheep's udder brought about through differences in nutritional planes in the first breeding year is reflected in its development in later years Lamb weight at weaning is related to lamb weight at birth and emphasizes the necessity for good nutrition of the pregnant ewe in order to produce lambs of good size and vitality

By weighing the offspring after each feed it was found that the milk yield of a large white sow over a 56 day lactation was 62 5 gal (284 4 l) When half the litter was kept under the cold and rather damp environmental conditions of the animal metabolism house they ate very little supplementary food, whereas the other half litter which had artificial heat ate a normal quantity and were superior pigs at weaning

No effect was observed on young pigs from birth to 12 weeks of age from the injection of an experimental liver extract

In the design and analysis of most of the experiments statistical treatment is introduced Experiments are also planned in order to test statistical theory This intimate association of experimentalist and statistician is of very considerable mutual benefit

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Forum

Interfacial Tension of Medicinal Paraffin/Water

The pendent drop shape method of measuring interfacial tensions whether using a camera or a microscope, would provide a simple and extremely sensitive means of detecting minute traces of water-adhesive impurities in *Nujol* and other liquids with negative spreading coefficients This is suggested by the fact that H W Douglas[1] obtained 52 dyne/cm for the interfacial tension of *Nujol*/water, while I found that 36 dyne/cm was the interfacial tension against water of some ordinary medicinal paraffin[2] the acid impurities of which were too slight to be detected by acid value determination

Incidentally, I should not have used the word 'pure' on p 88, line 5 of the right hand column in referring to my sample, which was taken from liquid supplied in bulk to the laboratory

S Mathews

Larkswood
Iver Heath
Bucks

(*Received, March 1950*)

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Miscellaneous Notes

UNIVERSITY APPOINTMENTS

London—Dr E K RIDEAL, F R S, has been appointed to the University Chair of Chemistry tenable at King's College from 1 August 1950

Manchester—Dr S C HARLAND, F R S, has been appointed George Harrison Professor of Botany and Director of the Botanical Laboratories and Experimental Grounds in succession to Professor E ASHBY He will take up his duties on 1 September 1950

AWARDS

Royal Astronomical Society—The gold medal of the Society has been awarded to Professor J STEBBINS, Director Emeritus of the Washburn Observatory, University of Wisconsin, and now Research Associate in the Lick Observatory, University of California

Royal Geographical Society—H M THE KING has approved the award of the Royal Medals as follows

Founder's Medal G F WALPOLE, Director, Department of Lands and Survey, Kingdom of Jordan, for contributions to the mapping of the Western Desert of Egypt,
Patron's Medal Professor H SVERDRUP, Director, Norwegian Polar Institute, for contributions to polar exploration and oceanographic investigations

The Council has awarded the Victoria Medal to Professor E DE MARTONNE, University of Paris, for studies in physical and regional geography

Institute of Metals—The first award of the W H A Robertson Medal has been made to W J THOMAS and W A FOWLER

ELECTION OF OFFICERS

Coal Utilization Joint Council—J S TURNER has been re-elected President and Sir JOHN CHARRINGTON Vice-President of the Council for 1950

Institute of Locomotive Engineers—R A RIDDLE, C B E, has been elected President for the session 1950–51

Institution of Mechanical Engineers—Names of members of Council announced at the Annual General Meeting include President, Dr S F DOREY, C B E, F R S, Vice-President, A C HARTLEY, C B E, and P L JONES, M C

Institute of Metals—The following officers have been elected for the year 1950–51 President, H S TASKER, Vice-President, Professor H O'NEILL and Professor F C THOMPSON Professor A J MURPHY has been elected senior Vice-President for the year and he will be the next nomination of the Council for the Presidency

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

Hydraulics Research Organization—The site chosen for the Research Station is at Howbery Park, near Wallingford It is hoped to move into the new buildings in the spring of 1951 In the meantime use is being made of facilities provided at the National Physical Laboratory and suitable University Departments

A model of the estuary of the River Forth is installed in the Hydraulics Laboratory at Teddington The major questions which have been investigated with the aid of this model are the effect on the regime of the estuary of constructing

i embankments to enclose lagoons into which dredged material would be dumped for reclamation
ii piers of the proposed Forth Road Bridge
iii dredging round the Beamer Rock to a depth of 45 ft (13 7 m) below Chart Datum
iv removing the Beamer Rock, a rock pinnacle in the middle of the river between the Forth Bridge and Rosyth, to 45 ft below Chart Datum
v extending the south arm of Rosyth Dockyard *a* in open construction at the shore end, and solid construction at the outer end, *b* in solid construction for its whole length

The reproduction of silting has proved extremely difficult, due to the low value of Reynold's number in the model, consequently the investigations have been largely based on an analysis of the past history of the estuary and a study of the tidal currents The experimental studies are being continued

Among the numerous investigations which have been undertaken is work in which data have been obtained about the relation between storms and coast erosion at Workington and Bridport This information will be available when the new laboratory is complete and large models can be constructed to study such problems on an adequate scale

BRITISH COAL UTILISATION RESEARCH ASSOCIATION

It has been found that certain simple organic substances with an ammonia base have a powerful action on coals of high volatile content, causing them to become dispersed in minute particles The particles are smaller than any that can be obtained by mechanical means In this state it will be possible to use the coal in various ways which have not so far been explored For example, when the dispersed coal is added to an excess of coal and is gently heated, it sets firm and has water repellant properties

The binding properties of these coal/solvent mixes can be used in the preparation of briquettes and also of special refractories

During the last year the B C U R A has devoted considerable effort to finding methods of burning bituminous coal without making smoke The work has included research on the mechanics of combustion of bituminous coal and the factors which affect the production of smoke in closed fireboxes In the past there has been a lack of accurate methods for estimating smoke, various instruments have now been devised and these should prove of value to member firms and other research organizations

During the course of some of these researches it was found that if certain gases were added to the air passing through the fuel under conditions of forced draught the formation of soot particles was greatly reduced Carbon dioxide, nitrogen and water vapour are all useful in this respect, and all of them are constituents of the flue gases Work on systems of recirculating the flue gases through the fuel bed is now progressing

On the recommendation of the Fuel Research Board, the D S I R has asked the B C U R A to make a study of the use of coal as fuel for gas turbines in a cyclone-type combustion chamber, this being so designed that the products of combustion are diluted with air to give gases at temperatures suitable for use with a gas turbine

INTERNATIONAL UNION OF CRYSTALLOGRAPHY

By kind invitation of the Swedish National Committee for Crystallography, the Second General Assembly and International Congress of the Union will be held in Stockholm, 27 June–3 July 1951 The programme has not yet been decided in detail but it is suggested that it might be generally similar to that of the Congress held at Harvard University in 1948 British crystallographers are invited to apply to Dr D C MARTIN, Assistant Secretary, The Royal Society, for further details

CORRECTION

We regret that Dr F A Vick was wrongly given as Dr V A Vick on p 135

New Books

A Survey of General and Applied Rheology

Second edition C W SCOTT BLAIR

(*xv* | *314 pp, 16 illus, 8½ in by 5½ in*)

London Sir Isaac Pitman and Sons Ltd, 1949 40*s* net

SINCE first published in 1943 this work has become the standard reference book of practical rheology The author is himself a well known pioneer in this field and the contents of Part II of the book, namely ‘Rheological Interpretation and the Evidence of Psycho-Physical Investigations’, are entirely his own creation, with the assistance of one or two co-workers. With his psychorheological investigations he has initiated a line of thought which may reach much further into the realm of physics Physics as the basic science of the external world starts from the picture of this world as conceived by human beings this picture is made up of sense impressions One has such sense impressions as ‘hot’ and ‘cold’, ‘light’ and ‘dark’, ‘firm’ and ‘soft’ Around these, the physicist builds up the branches of physics called Heat, Light, Rheology *etc* Then he proceeds to dehumanize them and Heat becomes ‘movements of particles’ and Light ‘waves of nobody-knows-what’ and Rheology ‘deformation of media’ *etc* Dr SCOTT BLAIR has shown in rheology that this is neglecting too much the other side of the sense impression relation *viz* the internal world, the basic science of which is psychology He has brought both worlds together in his particular field and made them human again, dedicating his book to Bill, the expert worker who judges by rule of thumb methods He has correlated these methods with the ‘pointer-readings’ to which EDDINGTON wanted to reduce physics

I have dealt first with the author's most original contribution To this is related his development of the Nutting equation, leading him into the philosophy of ‘dimensions’ in which he has recently been seconded by Professor DINGLE, *Phil Mag.* [7] 51 (1949) 94 I understand that Dr SCOTT BLAIR is publishing a book dealing extensively with this philosophy under the title of *Measurements of Mind and Matter* (Dennis Dobson Ltd, London) Lest the reader should get the impression that this *Survey*, which I have called the rheologists' handbook on practical rheology, is more philosophical than practical, let me emphasize that Part I of the book, on ‘Rheological Phenomena and their Measurement’, is of an entirely different character. It can confidently be said that not a single rheological phenomenon mentioned in the most obscure corner of the scientific world, including Russian publications, has escaped attention and is not here recorded The same applies to methods of measurement for which the most exhaustive references are given It is hardly necessary to draw the attention of the rheologist to this invaluable feature of the book As a matter of fact, there rarely appears a paper on a rheological subject in which the first edition of this book is not quoted All rheologists in general will need this second edition which has doubled the size of the book and includes everything which rheology has acquired between 1943 and 1949

M Reiner

Biometrical Genetics, The Study of Continuous Variation

K MATHER

(*ix+162 pp, 16 illus, 33 tables, 8½ in by 5½ in*)

London Methuen and Co Ltd, 1949 18s net

This book does not, as its title might imply, attempt to discuss the whole range of biometrical genetics, but is devoted primarily to the exposition of certain ideas of the author One category of these is concerned with the nature of the biological system on which continuous variation depends Previous authors have supposed that the numerous genes concerned are essentially similar in nature to other genes Mather, however, suggests that we are dealing with a special category of genes which he names 'polygenes' He originally supposed that these differed qualitatively from the major genes ('oligogenes') in that they consisted of heterochromatin rather than euchromatin, but this idea has had to be given up and he now seems hard put to it to argue that his polygenes are sharply differentiated from oligogenes, or differ in any appreciable way from the 'multiple factors' which have been a commonplace in genetical thought for many years

More importance, perhaps, attaches to emphasis which Mather places on the existence of linkage between groups of genes concerned with continuous variation Linkage is a general phenomenon, and is obviously a factor to be reckoned with in this connection But its importance will vary with the circumstances It is likely to be more important in organisms, such as the *Drosophila* studied by Mather, in which the number of chromosomes is small ; and it will be important in inbred and highly selected lines, from which disadvantageous genes which are not closely linked with advantageous ones will have been largely eliminated , it appears much more doubtful that it is also important in the relatively random-mating outbred populations with which the practical animal breeder is concerned. It is unfortunate that Mather does not attempt any discussion of these points

The greater part of the book is devoted to the elaboration and application of Mather's own statistical technique for the analysis of variance in crosses This is based on the consideration of a cross between two relatively pure lines and is thus, in the first place, applicable only to plants since such lines are not usually procurable in animals However, the simpler situation allows the analysis to be pushed somewhat further Mather works out several examples in detail and demonstrates the power and precision of his approach if it can be confronted with suitable data in relation to which Mather's assumptions as to gene action are justified His discussion of some of the general considerations to be borne in mind, for instance the problem of appropriate scaling, is particularly valuable It remains to be seen, however, whether the new refinements of biometrical technique can actually be used to produce results of practical value , occasionally (for instance, in the derivation of 'discriminant functions') technique seems to be in danger of outrunning practice and becoming an end in itself

C H Waddington

General Cytology

E D P DE ROBERTIS, W W NOWINSKI and F A SAEZ

Translated by W ANDREW

(*xi+345 pp, 149 illus, 9 in by 6 in*)

Philadelphia and London W B Saunders Co , 1949

$5 50 or *27s 6d*

What is General Cytology ? It is apparently the sum total of what can be learnt of the cells or from the cells of plants and animals The subject is large and heterogeneous Three authors are probably the least number that are needed to cover it and even these three have not seriously considered the plant cell save at the chromosome level where the subdivision between plant and animal so largely lapses.

Another subdivision of the subject is made manifest by this work that between technique and theory. Techniques give a kind of unity at least to the study of the animal cell and there are accounts of a great variety of techniques in this book Photography is dealt with in many of its new aspects ultraviolet, electron and phase-contrast as well as darkfield New methods of fixation and staining, sectioning and micromanipulation are discussed and illustrated.

It is too early to expect a corresponding theoretical unity between the observations and experiments derived from this variety of techniques The theoretical side is indeed somewhat bald and disconnected even in the field of the chromosomes to which genetics has given both a mechanical and physiological unity Cell division, and particularly cell division in Protozoa, where the nucleus and the cytoplasm and its organellae attain a momentary but significant cooperation, is not very well described Misprints are many and sometimes baffling **Mendel** toiling with peas in 1885, **Correns** labouring with '*Brysonia*', **Beadle** studying 'a hybrid of *Zea euchlaena*', would present a beginner or a zoologist with several insoluble problems Translation (from the Spanish) would also lead to difficulties for beginners who might not realize that 'Equilibrium of the Genes' is what **Bridges** and everyone else has called 'genic balance' In the method of introducing and defining large numbers of terms some of which (like telomere or karyokinesis) are not used outside books, this book is no worse than many others Such terms are no doubt a godsend to examiners and students alike in enabling them to go through the pantomime of asking and answering with decorum examination questions which neither party understands They are however a hindrance to knowing the subject—a purpose which a few students will, we hope, always have in view

These various defects however (if borne in mind) do not deprive the book of value for workers in the field of animal cytology it shows what kind of work is being done and also how to set about it Its figures are good, its bibliographies excellent

C D Darlington

Isotopic Carbon Techniques in its Measurement and Chemical Manipulation

M CALVIN, C HEIDELBERGER, J C REID, B M TOLBERT and P F YANKWICH

(*xiii+376 pp, 107 illus, 9 in by 5¾ in*)

New York · John Wiley and Sons Inc, 1949 $5 50
London Chapman and Hall Ltd, 1949 33s net

This handbook, by several members of the Radiation Laboratory of the University of California, summarizes in a relatively brief and manageable form the work which has been done so far in the use of carbon isotopes for tracer purposes. As is natural from the state of the subject, one of preparation rather than of achievement, it deals almost entirely with methods of measurement and with the preparation of marked compounds It is intended not so much for the student, who will find it hard reading, as for the investigator for whom it offers a survey of the original papers The methods are often abstracted in considerable detail, in fact frequently in sufficient detail to enable the preparation to be repeated without reference to the original paper It will thus be very helpful to investigators in planning their work to have a bird's-eye view of the various methods of introducing isotopic carbon into compounds which have been used It is to be hoped, however, that this will not deter them from trying many other methods

About a third of the book is devoted to the synthesis of C^{14}-labelled compounds and this section is followed by a brief discussion of some degradation procedures These are used to determine which carbon atoms of a compound are labelled, and some bio-synthetic methods of preparation of complex compounds are also included

The preliminary chapters on radioactive measurements will, I imagine, be suitable for reference to supplement actual experience in a physics laboratory It is difficult to see, however, who would make use of details such as the circuit diagram for the Lindemann electrometer, which is given It seems to be assumed that the investigators in this field will have a practically negligible knowledge of physics ! I suppose this is the logical consequence of modern tendencies towards specialization and the use by more or less unqualified people of delicate physical instruments as tools, in the same way as we use stop watches without bothering about their construction—a tendency illustrated by the recent offer of Geiger-Muller counters by a New York store at bargain prices

All this work is preparatory to the real objective of using labelled compounds for exploring the metabolic transformations of substances in living tissues It will be clear that this phase of the work is in a very preliminary state The authors wisely avoid giving details of those experiments in this direction which have been carried out—experiments which will be superseded in a short time—and content themselves with a bibliography which is complete to 1948

J A V Butler

Books to Come

Advanced Organic Chemistry Vol I G M DYSON (*1,000 pp; illus; royal 8vo*) London Longmans, Green and Co Ltd *63s* net

Die theoretischen Grundlagen der analytischen Chemie G. HÄGG (*200 pp, 26 illus*) Basel : Verlag Birkhauser *c Fr 20 00*

RESEARCH SUPPLEMENT

Crystal Chemical Considerations of the Surface Chemistry of Silica

W A WEYL, Dr Ing

The structure of silica and of all of the known silicates is governed by three principles 1 silicon is tetravalent in all crystalline compounds with oxygen, 2 it is always surrounded by precisely four oxygen ions, 3 the SiO_4 *tetrahedra, the universal building units of the various modifications of* SiO_2 *and of the natural and synthetic silicates, may be interlinked by having one common oxygen ion, but they cannot share more than one corner In the surface of* SiO_2 *at least one of these rules must be violated A possible surface structure is discussed and some of its unusual chemical reactions are derived Freshly broken* SiO_2 *tears apart an oxygen molecule from the air and produces active atomic oxygen Dehydration of silica gel cannot result in anhydrous silica according to the formula* $H_4SiO_4 = SiO_2 + 2\,H_2O$, *but removal of protons occurs These processes are strongly affected by impurities as well as by radiation*

SURFACE phenomena of silicates are becoming increasingly important in the field of catalysis With the exception of the base exchange phenomena characteristic of clay practically nothing is known about the chemical properties of silicate surfaces Our present knowledge of the surface chemistry of glass has been reviewed recently by WEYL[1] The complexity of glasses, however, makes an atomic interpretation of catalytic properties exceedingly difficult For example, it is impossible to predict whether the alkali concentration of a glass surface increases or decreases on heating because temperature affects the rate of three different processes, one of which brings alkali to the surface and the other two of which reduce its concentration through volatility and formation of alkali compounds

For a complete understanding of surface reactions one has to start with pure silica

It is the object of this paper to apply crystal chemical principles to the surface structure of SiO_2 and to derive its chemical properties from atomic structure The structure of the SiO_2 surface is derived from the dehydration of silica gel and from the fracture of a crystalline or vitreous modification of anhydrous silica

The principles which are applied to this problem are well established in the crystal chemistry of silicates and were worked out by BRAGG, GOLDSCHMIDT, WARREN and other workers in the field of atomic structures In addition to the principles which govern the atomic structure of crystals it is essential for the understanding of surface phenomena to consider the strong polarization effects which result from asymmetrical force fields For this purpose the rules of polarization of FAJANS are the guiding principles

Surface structures are defect structures Classical crystal chemistry does not take into consideration the fact that each crystal must have surfaces but treats crystals as symmetrical arrays of ions which extend infinitely in space The parameters commonly used for describing a crystal structure, such as internuclear distance, coordination number and symmetry, apply to the average atom but not to atoms in the surface

PRINCIPLES OF THE ATOMIC STRUCTURE OF SILICATES

The atomic structures of silicates are treated in several textbooks They are governed by three basic principles

1 in the condensed state (crystals, glasses, aqueous solutions and fused salts) silicon in combination with oxygen has the valency of four

2 the modifications of silica and of silicates reveal that the Si^{4+} ion is always surrounded by precisely four oxygen ions The SiO_4 tetrahedron seems to be the universal building unit of all natural and synthetic silicates, including silicate glasses

3 the SiO_4 tetrahedra may be interlinked in a great variety of patterns They may form chains, double chains, ring structures or three dimensional networks In spite of this variety of arrangements in space, two SiO_4 groups have never been found to have more than one oxygen ion in common Two tetrahedra may share a corner but never a face or even an edge

These principles result from the stability of the electron configuration of the Si^{4+} (complete octet shell) and its strong positive force field The high charge of the small silicon ion is responsible for the strong Coulomb forces which its ions exert upon the O^{2-} ions and which lead to the stability of the SiO_4 tetrahedron The combination of strong force field and low polarizability of the Si^{4+} is responsible for the third principle Two SiO_4 groups sharing a face or even an edge would make the energy content of this unit too high to remain stable because strong repulsion forces exist between two Si^{4+} ions in close proximity Sharing an edge would decrease their distance to 58 per cent of that necessary for sharing a corner In order to share a face instead of a corner of their tetrahedra the two central Si^{4+} ions would have to approach to one third of the original distance

The high stability of the SiO_4 group may be judged from the extremely low vapour pressure of SiO_2 in the absence of water Dry SiO_2 would have to form O—Si—O molecules in order to vaporize and thus would lose its fourfold coordination In the presence of water this is not necessary because the hydrated silica molecule $Si(OH)_4$ satisfies the conditions of the second principle

The tendency to form SiO_4 groups is so strong that it causes the silicon monoxide to disproportionate on cooling SiO, the lower oxide of silicon, exists in the vapour phase, where it has been found spectroscopically by BONHOEFFER[8] On cooling the SiO molecule, the electronic structure of which probably corresponds to that of carbon monoxide, apparently is torn apart in order to satisfy the fourfold coordination of silicon The condensation product still has the chemical composition of SiO but it is amorphous and consists probably of SiO_4 tetrahedra and elemental silicon Its chemical reactions are those of silicon , it forms $SiCl_4$ with chlorine and liberates hydrogen from a sodium hydroxide solution

Keeping these facts in mind one can now derive the atomic structure and chemical properties of the silica surface Some reflection on the surface structure of SiO_2 leads to the conclusion that the surface must violate at least one of the three principles which govern the structure of the interior of the crystal

If the silicon were to change its valency from four to two, its positive force field would be much weaker and it would be less necessary for its stability to maintain fourfold coordination The high charge of Si^{4+} makes it difficult for it to enter interstitial positions and thus make oxygen ions available in the surface The relatively high polarizability of the large oxygen ion as compared with the small silicon ion makes it imperative that the surface be formed by oxygen ions alone The mobility of the surface atoms makes it possible for the O^{2-} ions to be pushed into the surface layer and for Si^{4+} to be pushed into the next layer This atomic arrangement leads to oriented dipoles which form the electrical double layer. The surface layer will rearrange so that the surface free energy of the system is lowered even at the expense of the lattice energy of the following atomic layers One sees from this point of view that the surface exerts a depth action and must be treated as a defective crystal It is not sufficient to consider only one or two atomic layers if one wants to derive surface properties

In order to develop a picture of the surface of silica we shall follow its formation One way to do so is to start out with an aqueous solution of a silicate or a hydrosol of silica and dehydrate it completely Another approach to the surface of SiO_2 is to break quartz or silica glass and discuss the atomic rearrangements which will take place at the freshly formed surface in order to conform as much as possible with the three principles

DEHYDRATION OF SILICA GEL

Silica gel is the polymerization product of $Si(OH)_4$ and is formed by hydrolysis of $SiCl_4$ or ethyl silicate, or by adding an acid to an aqueous solution of alkali silicate Orthosilicic acid polymerizes fast, but the aggregation slows down as the size of the molecules increases Even if the gel has formed, the process continues (aging of gel) and in its final stage it leads to the mineral opal which then shows the beginning of crystallization to cristobalite

The polymerization of $Si(OH)_4$ progresses through a number of stages which are characterized by different optical and mechanical properties All forms, however, follow the three principles in their atomic structures Silica gels have an extremely large surface The surface elements may be conveniently described by the formula

$$\left\{Si^{4+}\left(\frac{O^{2-}}{2}\right)_3 OH^-\right\}(H_2O)_x \qquad (1)$$

which indicates that each Si^{4+} ion is surrounded by four oxygen ions , three of them are shared with neighbouring Si^{4+} and consequently count as one half of ½(O^{2-}) The fourth oxygen ion is shared with a proton *i e* it is part of the hydroxyl group which is left from the monomer $Si(OH)_4$ These OH^- groups are responsible for the water content of the gel because they are able to retain neutral H_2O molecules by means of hydrogen bonds (hydronium ions, H_3O^+)

Heating a silica gel causes it to lose its adsorbed water If the temperature is sufficiently high the hydronium ions of OH^- groups become unstable and finally anhydrous silica SiO_2 is formed Formally the last step of dehydration can be described as

$$2\left\{Si^{4+}\left(\frac{O^{2-}}{2}\right)_3 OH^-\right\} \xrightarrow{\Delta} 2\left\{Si^{4+}\left(\frac{O^{2-}}{2}\right)_4\right\} + H_2O \qquad . \ (2)$$

A little reflection, however, will lead to the conclusion that this process is not likely to occur because two neighbouring silicon ions, already linked together by one O^{2-}, would then have to share a second oxygen ion In other words the final step of dehydration of silica gel would cause the surface tetrahedra to have edges and not only corners in common , an atomic arrangement which violates the third principle and consequently would be highly improbable

According to our findings the final step in the dehydration of silica gel can be described as follows

$$\left\{ Si^{4+} \left(\frac{O^{2-}}{2}\right)_3 OH^- \right\}(H_2O)_x$$

$$\xrightarrow{\Delta} \left\{ Si^{4+} \left(\frac{O^{2-}}{2}\right)_3 O^{2-} \right\}^- + H_3O^+ + (x-1)\,H_2O \qquad (3)$$

With the removal of the last water of hydration, not the OH^- groups but only protons or hydronium ions are removed, thus leaving the Si^{4+} with its complete coordination (second principle) and without forcing it to share another O^{2-} with one of its neighbours From the reaction scheme above two features are obvious The water vapour which is driven off from the gel at high temperatures must give an acid reaction Furthermore the reaction leads to electrically charged products The vapour phase carries an excess positive charge and the solid has a negative charge

In addition there is another feature which is less obvious The interior and the exterior building unit of silica gel, namely $\{Si^{4+}(\frac{1}{2}O^{2-})_4\}$ and $\{Si^{4+}(\frac{1}{2}O^{2-})_3OH^-\}$, can be described by a chemical formula of stoichiometric composition SiO_2 and $SiO_2 \cdot \frac{1}{2}H_2O$ This is not possible for the new surface unit The formula of $\{Si^{4+}(\frac{1}{2}O^{2-})_3O^{2-}\}$ would have to be written as $SiO_2 \cdot \frac{1}{2}O$, which means that the surface contains excess oxygen ions Such a surface unit, an ' E-unit ', is not a normal constituent of the crystal lattice but its excess oxygen makes it a defect

From the structure of the ' E-units ' one sees that the one oxygen ion is exposed to only one Si^{4+} and has no balancing positive field at its other side

The surface units have a dipole moment and all dipoles are oriented so that their centres of positive charge point towards the interior and their centres of negative charge point towards the exterior of the particle, an orientation which produces an electrical double layer

These ' E-units ' can be stabilized by adsorbing positive ions or polar molecules which can balance the force field and restore some of its original symmetry. Besides the electrical compensation the ' E-units ' are likely to undergo an electron transfer leading to divalent silicon and atomic oxygen

$$\left\{ Si^{4+} \left(\frac{O^{2-}}{2}\right)_3 O^{2-} \right\}^- \longrightarrow \left\{ Si^{2+} \left(\frac{O^{2-}}{2}\right)_3 \right\}^- + O \qquad (4)$$

Under the influence of the positive field of the Si^{4+} the two valency electrons of the O^{2-} ion are pulled over to the Si^{4+} and change it into Si^{2+} Atomic oxygen is liberated as the result of this electron transfer By decreasing the positive charge the silicon atoms of the surface area are satisfied with incomplete coordination

The final step of dehydration of silica gel can be described as follows

a the water removed from silica gel by heating contains protons or hydronium ions with positive charges which are not balanced by anions the water vapour gives acid reactions and has an excess positive charge

b units are formed in the surface layer of dehydrated silica gel which have an excess of oxygen over the stoichiometric ratio The gel assumes a negative charge during the last phase of its dehydration

c the surface structure of dehydrated silica gel is likely to release atomic oxygen and to form Si^{2+} ions, thus leading to a molecular film of silicon monoxide or to its product of disproportionation—elemental silicon

SILICA DUST

In quartz as well as in the high temperature modification of silica, including glass, the three principles governing the structure of silicates demand that each Si^{4+} ion should share all its oxygen ions with four others The surface, however, contains some Si^{4+} ions which cannot have fourfold coordination

The surface of a freshly broken quartz crystal has to readjust itself in order not to violate one of the three structural principles The only way to conform with the demands of the three principles consists in a chemical reaction with the environment, for example, with oxygen or water molecules If sufficient H_2O is available at the moment fracture occurs the energy requirements for producing a new surface are considerably decreased No measurements are available for the influence of water on the crushing strength of pure SiO_2 but it has been found that the energy necessary to cleave mica[2] amounts to 2,500 ergs *in vacuo*, but to only 375 ergs in air for each sq cm of fresh surface Even in the best obtainable vacuum there are sufficient gas molecules available for reacting with the new surface within a very short time

Figure 1 is a schematic picture of a crystallized and b vitreous forms of SiO_2. Following its fracture one can distinguish two types of Si^{4+} ions. One type retains its complete fourfold coordination, but the other one cannot. The first type has an excess of oxygen ions over the stoichiometric ratio because it shares only three of its four oxygen ions with neighbouring Si^{4+}, whereas the stoichiometric formula of silica, $\{Si^{4+}(\frac{1}{2}O^{2-})_4\}$, demands that it share all four oxygen ions in equal parts with other Si^{4+} ions. Not only has this Si^{4+} an excess of oxygen but also an excess negative charge, as can be seen from its structural formula $\{Si^{4+}O^{2-}(\frac{1}{2}O^{2-})_3\}^-$. It is the same structural element which was called 'E-unit' in the preceding section.

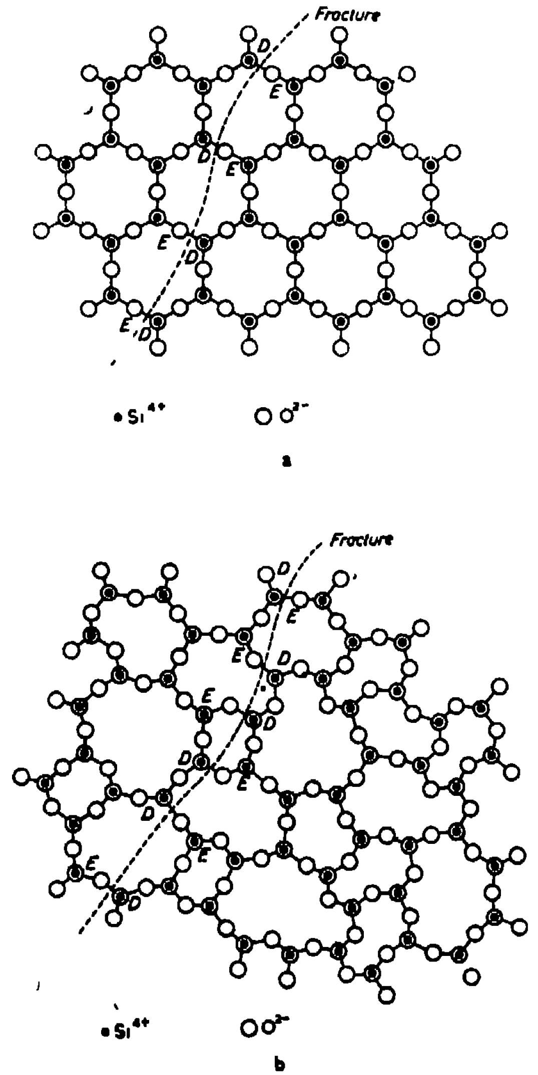

Figure 1 *Fracture of a quartz and b vitreous silica indicating the formation of E and D centres*

At the other side of the fracture one finds an Si^{4+} which has an oxygen deficiency and an excess positive charge. It has incomplete coordination because it has only three O^{2-} ions and all three are shared with other Si^{4+} ions $\{Si^{4+}(\frac{1}{2}O^{2-})_3\}^+$. It will be called the 'deficiency' or 'D-unit'.

These centres of oxygen excess and oxygen deficiency are formed in precisely equal numbers. Also there is no obvious reason for finding more of one kind at one fractured particle and more of the other at another particle. Therefore, dust particles will have the stoichiometric composition and be electrically neutral. However, each of the two centres can undergo a change.

E-centres contain an oxygen ion in a state of one-sided polarization. The positive force field of the Si^{4+} pulls over its valency electron and if it succeeds in doing so atomic oxygen is released from the E-centre under formation of an E′-centre and atomic oxygen

$$\left\{Si^{4+}O^{2-}\left(\frac{O^{2-}}{2}\right)_3\right\}^- \longrightarrow \left\{Si^{3+}\left(\frac{O^{2-}}{2}\right)_3\right\}^- + O \tag{5}$$

This process is greatly enhanced by irradiation. It leads to atomic oxygen without affecting the electric charge of the E-centres.

For each E-centre formed in the new surface there has to be a D-centre as its counterpart. D-centres are Si^{4+} ions with incomplete coordination and an excess positive charge. Consequently the D-centres attract and combine with constituents of the atmosphere

$$\left\{Si^{4+}\left(\frac{O^{2-}}{2}\right)_3\right\}^+ + H_2O$$
$$\longrightarrow \left\{Si^{4+}\left(\frac{O^{2-}}{2}\right)_3 OH^-\right\}^0 + H^+ \tag{6}$$

In a moist atmosphere D-centres attract water molecules and combine with their OH^- groups, thus releasing protons. This step neutralizes the excess positive charge of the D-centres and complies with the demands of the second principle (fourfold coordination) without violating the third (sharing of corners only).

The other possibility is the reaction of D-centres with oxygen of the atmosphere to form E-centres and atomic oxygen The two electrons necessary for this step

$$\left\{Si^{4+}\left(\frac{O^{2-}}{2}\right)_3\right\}^+ + O_2 + 2e \longrightarrow \left\{Si^{4+}\left(\frac{O^{2-}}{2}\right)_3 O^{2-}\right\}^- + O \qquad (7)$$

have to be supplied by the defective surface layer , this amounts to the release of an oxygen atom and the formation of another defect in a deeper layer The probability of this process taking place is greatly increased by radiation as was shown by Weyl and Forland[4]

Formation of a new surface by crushing silica in a dry atmosphere leads to particles which release atomic oxygen In order to comply with the rigid demands of the structural principles the surface ions must undergo a rearrangement Only a part of the disturbance created by a surface can be compensated for by unusual atomic groupings, such as interstitial Si^{4+} or three tetrahedra having one common corner Some of the Si^{4+} ions will be left with excess oxygen ions and others with a deficiency These centres enter into chemical reactions with the environment During these reactions some of the Si^{4+} ions will be reduced to either Si^{2+} or elemental silicon

CONCLUSIONS AND SUMMARY

It has been demonstrated that the surface of silica offers some unique chemical features which can be derived from the principles governing the atomic structure of silicates under application of Fajans' rules dealing with the polarization of ions, especially in strongly asymmetrical force fields One of the features consists in the formation of atomic oxygen at the surface of freshly crushed silica, or of silica gel during its dehydration This phenomenon is rare but not unknown in inorganic chemistry , it can be observed during the oxidation of elemental phosphorus at low temperatures It is more common for organic compounds when they are oxidized at relatively low temperatures, especially when irradiated with ultraviolet light In a forthcoming publication by Weyl and Enright experiments will be described using a sensitive colour indicator for atomic oxygen which prove that atomic oxygen is formed if quartz is crushed Other experiments using the oxidation of silver ions or metallic silver to the higher oxide of silver, Ag_2O_3, demonstrate the high oxidation potential of the atomic oxygen at the silica surface. It has been suggested by Weyl[5] that it is this atomic oxygen at the surface of freshly crushed silica which is the cause of its toxic effect In spite of the apparent inertness of silica and the non-poisonous nature of soluble silicates it has been proved beyond any doubt that silica dust causes a specific type of pneumokoniosis (silicosis) the causes of which are still unknown Early attempts to attribute silicosis to the sharpness of crushed silica failed when it was found that the sharp dust particles of silicon carbide did not produce this disease Sosman[6] wrote on this subject as follows ' It is clear now that this is not the explanation, but that finely divided silica in the lungs is a kind of chemical poison It is about the last substance on earth that the chemist would have suspected of being poisonous, for it is so universally distributed that we all eat it and breathe it all our lives '

The puzzling feature, however, is that soluble silicates (dust of cement plants) neither cause silicosis nor interfere with the metabolism of plants and animals Furthermore, ' old dust ' of silica seemed ineffective so that the typical cause of silicosis is ' freshly crushed ' silica

Another unique feature of the silica surface is its ability to donate protons in the presence of water Dehydration of silica gel by heating in air produces water vapour containing protons or hydronium ions As the charges of these protons are not balanced by anions, both vapour and dehydrated gel have excess electric charges, the vapour being positive and the gel negative

The chemical mechanism of oil cracking has been explained by Turkevich and Smith[7] who postulated that the catalyst must provide the protons Hansford[8] proved that deuterium oxide adsorbed on cracking catalysts exchanged deuterium for hydrogen at temperatures far below those of cracking He also found that the industrially used catalysts (silica in combination with aluminium oxide) have a concentration of protons on their surfaces which is higher than that of pure silica Most industrial cracking catalysts are based on natural and synthetic hydrated alumino-silicates Recent developments[9] in the field of cracking catalysts show that silica-magnesia combinations have properties which are superior in some respects to those of silica-alumina catalysts

For pure silica the mechanism of hydrogen ion donation has been elucidated and the role of additional oxides shall be treated in a later publication

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School of Mineral Industries
The Pennsylvania State College

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Influence of Interfacial Potential on Friction and Surface Damage

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An experimental study has been made of the influence of interfacial potential on the friction and surface damage of inert metals, such as platinum, immersed in an electrolyte It is shown that small changes in the interfacial potential have a profound effect, both on the friction and on the surface deformation The friction is a minimum in the region of oxygen deposition, rises to a maximum at a potential of c 0 3 volts on the H_2 *scale and falls again in the region of hydrogen deposition The results are explained in terms of the electrodeposition and electrosolution of adsorbed gas layers and also of the electrical interaction of the charged double layer*

IT is well known that the adsorption of a layer of gas on the metal surface may have a profound effect on the friction[1] and in this connection it is interesting to consider the friction of metals which are immersed in an electrolyte If an inert metal such as platinum is immersed in an acid electrolyte it is possible, by suitably varying the interfacial potential, to bring about the electrodeposition of either hydrogen or of oxygen When the interfacial potential is in the region of + 1 0 v on the hydrogen scale (the metal being positive) the electrode surface becomes covered with a monolayer of oxygen, and if the potential is made more positive still, oxygen is evolved, and we are in the region of oxygen overpotential As the interfacial potential is reduced below about + 1 6 v the monolayer of oxygen is removed and, in the region of 0 v on the hydrogen scale, a monolayer of hydrogen is deposited[2] If the potential is made more negative still, hydrogen is evolved and we are in the region of hydrogen overpotential In the intermediate region of potential, that is, round about 0 2 to 0 6 v on the hydrogen scale, the electrode surface should be reasonably free from either oxygen or hydrogen, *Figure 1*

It would clearly be of interest to investigate the friction of metal surfaces in an electrolyte at different interfacial potentials Several workers have reported changes in the friction between a metallic surface and some other material such as glass or chalk as the metal surface was polarized Such effects were first demonstrated by EDISON[3] and subsequently studied by KOCH[4], WAITZ[5] and KROUCHKOLL[6] It has also been shown[7, 8] that the friction of immersed solids is dependent upon the hydrogen ion concentration of the solution The results, however, cannot be easily interpreted since the interfacial potentials of the surfaces are not clearly defined

Some preliminary measurements of the friction of platinum, as the interfacial potential is varied under controlled conditions, were made by BARKER[9] (1947) and the investigations have recently been continued The friction is measured between a stretched platinum wire and a platinum cylinder, weighing about 2 gm, which can slide on it These are contained in a glass cell which can be freed from gas and filled with an electrolyte A large platinized platinum electrode serves as the polarizing electrode through which a current can be passed to the wire and cylinder, and the interfacial potential of the wire and cylinder can be measured against a reversible hydrogen electrode immersed in a similar electrolyte The whole cell can be rotated so that the wire can be tilted through 180° The angle at which sliding occurs gives a measure of the friction.

It was found that great care must be taken to free the system from traces of impurity, but when this was done results similar to those shown in

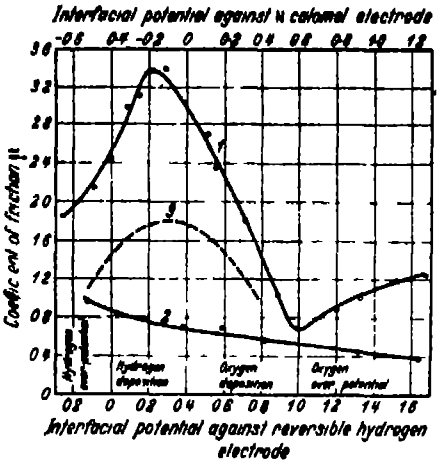

Figure 1 Curve 1 Friction between platinum surfaces immersed in an acid electrolyte as the interfacial potential is changed The friction is a minimum at the potential of oxygen deposition (+ 1 0 volt), reaches a maximum at the potential ≏ + 0 3 v and falls again in the region of hydrogen deposition Curve 2 Solution contaminated with a trace of H_2S *Curve 3*[10] *Surface tension (arbitrary units) between platinum and electrolyte*

Figure 1 were obtained Curve *1* shows the average results for a series of experiments for the static friction of platinum on platinum in pure dilute sulphuric acid (0 1 N) It will be seen that the changes in friction as the potential is varied are very great indeed In the region of + 1 0 v, which corresponds to oxygen deposition, the coefficient of friction μ = 0 7 As the potential is decreased and the oxygen is removed, the friction rises and in the region of 0 3 v has reached a value of μ = 3 4 As the potential is reduced below this, and we come into the region of hydrogen deposition, the friction falls to a value of μ = 2 3 At still more negative potentials, that is, in the region of hydrogen overpotential, there is a further decrease, but the friction is still high (μ = 2) compared with the values obtained in the region of oxygen deposition (μ = 0 7) It will be seen that in the region of oxygen overpotential *i e* as the surface becomes more positive than + 1 0 v, there is a small increase in the friction The reason for this is more complex and will not be discussed here

The change in friction with potential is accompanied by a corresponding change in the damage to the surface *Figure 2* shows the tracks formed on a flat platinum surface when a small curved platinum slider passes over it once under a load of 20 gm *Figure 2a* shows the damage when the interfacial potential is *c* 1 0 v and the friction is a minimum the surface damage is slight *Figure 2b* shows the corresponding damage when the potential is *c* 0 3 v and the friction is a maximum In this region there is profound damage, welding and seizure of the metal It is frequently found that the surfaces stick together at this potential so that the coefficient of friction cannot be measured

If a trace of impurity is present, these high frictions are not observed Curve 2, *Figure 1*, shows the results obtained when the solution is contaminated with a trace of H_2S The friction stays at a comparatively low value over the whole potential range This suggests that the nature of the film on the surface can be more important in determining the friction than the value of the interfacial potential itself

These results are consistent with the observations on the friction of outgassed metals The accumulation of a monolayer of oxygen on the surface reduces the friction to a low value A film of hydrogen is much less effective as a lubricant than the corresponding film of oxygen In the intermediate region, where neither is present, the friction is very high indeed

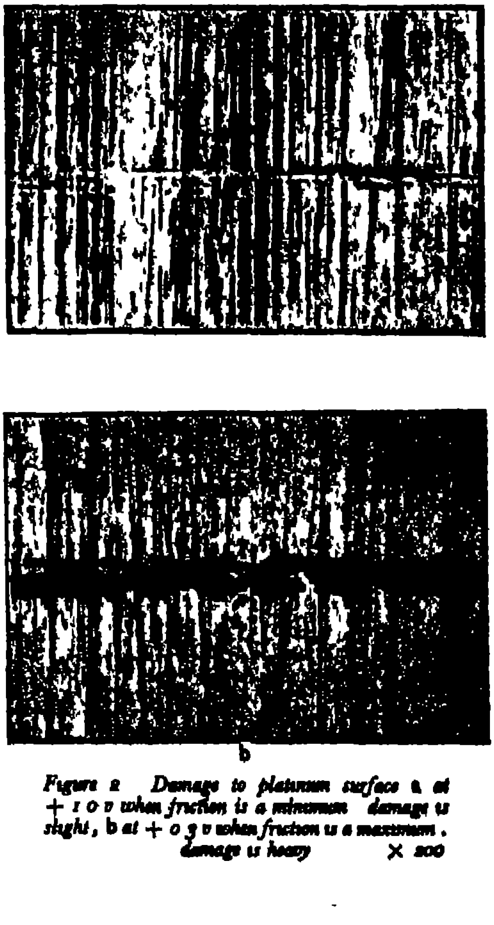

Figure 2 Damage to platinum surface a *at + 1 0 v when friction is a minimum damage is slight,* b *at + 0 3 v when friction is a maximum. damage is heavy × 200*

and seizure may readily occur when the surfaces are placed in contact. Apparently water itself is a very poor lubricant.

FRICTION AND SURFACE TENSION

It is well known from electrocapillary curves that the surface tension at a mercury surface in contact with an electrolyte is dependent upon the interfacial potential If, for example, a mercury surface is placed in contact with a dilute solution of sulphuric acid containing a few mercury ions the surface of the mercury will be positively charged These charges on the surface will mutually repel one another and will reduce the surface tension If the interfacial potential is made less positive by applying a polarizing current (or in any other way) the surface tension will rise as the positive charge on the surface is reduced and will reach a maximum when the surface charge is zero Further reduction in the interfacial potential will result in the accumulation of electrons on the mercury surface and the mutual repulsion of these will again decrease the surface tension Corresponding to the charge on the surface, positive or negative ions will be attracted from the solution to form the electrical double layer and these also will influence the surface tension With a mercury surface in 0 1 N H_2SO_4 the maximum of the electrocapillary curve would be approximately + 0 56 on the N calomel electrode, and at this point there should be effectively no charge on the surface

For platinum we cannot measure the surface tension direct, but Frumkin, Gorodetskaja, Kabanow and Nekrasow[10] have measured the contact angle between a gas bubble and a platinum surface immersed in 0 1 N Na_2SO_4 solution and have shown that it is a maximum (corresponding to maximum surface tension between the platinum and the electrolyte) when the interfacial potential is in the region of 0 on the calomel scale (+ 0 28 on the hydrogen scale) Their results are plotted on curve 3, *Figure 1* It will be seen that the position of maximum surface tension corresponds roughly to the position of maximum friction.

Since the surface tension is a measure of the attractive force between the metal atoms and the friction is due to the attraction between the metal atoms on the two adjacent surfaces (with consequent localized adhesion) we might expect to find a correlation between them and it is interesting to see that this is so

In general, we have two effects operating The first is the presence on the surface of gas or other films which may reduce the friction If these films are removed when the interfacial potential is changed there will be a corresponding change in the friction *cf* oxygen If they are not removed and the films are effective lubricants, the friction may remain at a low value even when the interfacial potential is changed *cf* H_2S, *Figure 1*, curve 2 In addition to this, there will be the effect of the electrical charge on the double layer at the interface If there is a concentration of positive charge (or of electrons) on the surface, the electrical repulsion will reduce the surface tension at the metal electrolyte interface At the same time the repulsive interaction between the electrical double layers will reduce the attraction and adhesion between the two metal surfaces and hence reduce the friction At the point where the surface charge is reduced to zero the surface tension will be a maximum and the adhesion and friction between the two surfaces will also be a maximum

This relation between the interfacial potential and the friction, adhesion and surface damage of solids is of considerable interest in connection with a number of other physical phenomena such as the variation of strength properties of solids in the presence of surface active materials or when immersed in electrolytes[11, 12]

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Nucleic Acids: Relationship between Ribo- and Deoxyribonucleases

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Evidence is presented which indicates that the mode of action of deoxyribonuclease on deoxyribonucleic acid is similar to the action of ribonuclease on ribonucleic acid. It appears however that the enzymes are quite specific. Factors governing the specificity of the enzymes are discussed and it is suggested that it is the pyrimidine bases of the nucleic acids which determine specificity. An analogy is drawn between the specificity of action of nucleases on the nucleic acids and the specificity of the action of proteinases on proteins.

THE action of ribonuclease from pancreas[1] on ribonucleic acid has been extensively investigated and is known to involve an initial depolymerization of the complex nucleic acid molecule into smaller units[2] which are then hydrolysed by the enzyme to lower polynucleotides. Although LORING and CARPENTER[3] claimed to have isolated the four mononucleotides following the hydrolysis of ribonucleic acid with ribonuclease, it is generally accepted that the products which result from the action of the enzyme are polynucleotides of varying molecular size[4]. Ribonuclease preferentially hydrolyses the pyrimidine nucleotide groups of ribonucleic acid and leaves a non-diffusible 'core', containing an increased ratio of purines to pyrimidines, which is resistant to further action of the enzyme[5, 6].

ACTION OF THE ENZYME

From recent studies[7, 8] it is concluded that the action of deoxyribonuclease[9] on deoxyribonucleic acid is closely analogous to the action of ribonuclease on ribonucleic acid. The evidence for this conclusion may be summarized as follows. When the hydrolysis of deoxyribonucleic acid by deoxyribonuclease is measured by the formation of acid soluble polynucleotides, an initial lag is observed. During this lag period there is a rapid fall in the viscosity of the deoxyribonucleic acid solution, which commences immediately after the addition of the enzyme, and is more or less complete before the liberation of acid soluble material occurs to any marked extent. It has been demonstrated that under the conditions employed, this fall in viscosity is due specifically to the action of the enzyme and not to the non-specific action of metallic ions[9, 10].

The changes in viscosity induced by the enzyme in solutions of deoxyribonucleic acid prepared by the method of MIRSKY and POLLISTER[11] are considerably greater than the changes induced in solutions of commercial, partially degraded sodium thymonucleate at the same concentration, but the solutions in each case have approximately the same final viscosity. Thus it is concluded that the action of deoxyribonuclease on deoxyribonucleic acid results initially in the depolymerization of the molecule into certain smaller units which are then hydrolysed to acid soluble polynucleotides by cleavage of internucleotide phosphate linkages.

These polynucleotides, which appear to be the end products of the action of the enzyme, have been partially separated by dialysis and ethanol precipitation into a series of fractions. Measurements of specific viscosity, rates of diffusion and dephosphorylation by prostate phosphatase have shown that these fractions vary in molecular size from possibly tri- or tetranucleotides to a relatively large, non-diffusible residue[12, 13]. The action of an excess of deoxyribonuclease on the latter fraction resulted in the liberation of pyrimidine, but not purine, mononucleotides and the formation of a non-diffusible residue which in agreement with ZAMENHOF and CHARGAFF[14], was resistant to further action of the enzyme and contained an increased ratio of purines to pyrimidines. In contrast, analysis of certain of the smaller polynucleotide fractions showed that these contained an increased ratio of pyrimidines to purines.

From these results it is concluded that deoxyribonuclease preferentially hydrolyses the pyrimidine nucleotide groups of the deoxyribonucleic acid molecule.

SPECIFICITY OF THE ENZYME

In view of the fact that the action of deoxyribonuclease on deoxyribonucleic acid so closely parallels the action of ribonuclease on ribonucleic acid, the specificity of the enzymes becomes of increased interest. The lack of any enzymic effect of crystalline ribonuclease on deoxyribonucleic acid led GREENSTEIN and JENRETTE[15] to the conclusion that each type of nucleic acid requires its own specific enzyme for depolymerization and that the molecular structure of each nucleic acid is fundamentally different. It is apparent that the specificity of the enzyme is not due to the differences in polymerization of the ribo- and deoxyribonucleic acids since the same specificity is observed when the partially degraded nucleic acids are subjected to the action of the enzymes. For example, experiments in collaboration with GILBERT have shown that if the hydrolysis of deoxyribonucleic acid by deoxyribonuclease is arrested at any stage, the resulting products are completely resistant to the action of ribonuclease.

Deoxyribonuclease was allowed to act for 20 minutes on a substrate of deoxyribonucleic acid in the presence of magnesium sulphate and veronal buffer (*p*H 7·0), and then the enzyme was destroyed by shaking the mixture several times with chloroform-octanol mixture (9 : 1) or by heating. Addition of more deoxyribonuclease to the substrate separated after this treatment resulted in further degradation of the deoxyribonucleic acid; but if, instead, heat treated ribonuclease was added, no further hydrolysis occurred (as shown by the formation of acid soluble material) of the nucleic acid in the substrate. We used heat treated ribonuclease to ensure that this enzyme was free from traces of deoxyribonuclease which is more labile to heat. Similarly, the products which are obtained when ribonuclease is allowed to act for a short time on ribonucleic acid cannot be degraded further by the action of deoxyribonuclease. This was shown by the fact that if ribonucleic acid in the presence of magnesium sulphate and veronal buffer (*p*H 7·0) was digested for 20 minutes with heat-treated ribonuclease and then shaken with chloroform-octanol mixture (9 : 1), subsequent addition of deoxyribonuclease to the separated substrate resulted in no further hydrolysis of the nucleic acid.

Theory of specificity— Undoubtedly, therefore, specificity of the enzymes is governed by differences in the structure and composition of the components of the two types of nucleic acid. In consequence, it may be of advantage to summarize briefly the differences between the pentose and deoxy-pentose nucleic acids which conceivably may determine the enzyme specificity.

The most obvious of these are the differences in the nature and structure of the sugar constituents. Although it is now apparent that for the pentose and deoxypentose nucleic acids the lactol ring is of the furanose form[16] it is possible that the glycosidic linkages may be of different types. In this connection, DAVOLL, LYTHGOE and TODD[17] by the application of the oxidative fission procedure to the glycosides, have shown that the base-sugar linkage of the ribonucleosides have the β-configuration. Although there is no similar information concerning the configuration at the glycosidic centres in deoxyribonucleic acid, a tentative analysis of the optical rotation data provided by DERIAZ, OVEREND, STACEY and WIGGINS[18] for the glycosides of 2-deoxyribose suggests that these linkages in deoxyribonucleosides may be of the α-type.

It does not appear that the phosphate linkages in the pentose and deoxypentose nucleic acids are of different types, since ZITTLE[19] has shown that the phosphoesterase from calf intestinal mucosa hydrolyses polynucleotides from both ribo- and deoxyribonucleic acids (but *cf* EULER and FONO[20, 21]). These linkages, however, may differ in the point of attachment to the sugar residue and thus confer specificity on the nucleases. The presence of the extra hydroxyl group at carbon atom number two of the *d*-ribose moiety in the pentose nucleic acids, for example, provides an alternative centre for phosphate linkage.

However, the fact that both ribonuclease and deoxyribonuclease liberate pyrimidine nucleotides preferentially from the respective nucleic acids suggests that the specificity of the enzymes is determined by the nature of the pyrimidine bases. This hypothesis is strengthened by the fact that the nucleic acids contain different pyrimidine bases, namely uracil in ribonucleic acid and thymine in deoxyribonucleic acid.

If it is tentatively assumed that the pentose and deoxypentose nucleic acids have the same type of internucleotide phosphate linkages *i e* a common 'backbone' structure, but differ in the nature of the pyrimidine 'side-chains', there is a distinct analogy between the specificity of the action of nucleases on the nucleic acids and the specificity of the action of proteinases on proteins. In the latter case it will be recalled from BERGMANN's[22] work that, although the proteinases effect the hydrolysis of peptide bonds common to the 'backbone' structure of all proteins, the individual enzymes exhibit a high degree of specificity in their action which is determined by the nature of the 'side chain' residue in the substrate. In a similar manner it may well be that the specificity of the nucleases is conditioned by the presence of a pyrimidine 'side chain' of particular structure or configuration. In this connection the observations of ZITTLE[23, 24] that the action of dilute sodium hydroxide on deoxyribonucleic acid effects partial deamination and renders the nucleic acid resistant to the action of the specific nuclease, serve to emphasize the importance of the structure of the bases on the enzyme-substrate reaction.

In conclusion it may be pointed out that this hypothesis offers an explanation why the products of the enzymic degradation of both ribo- and deoxyribonucleic acid are not homogeneous, but exhibit a wide range of molecular size. Recent investigations[25–28] shew conclusively that not only do the analytical figures for different nucleic acids fail to approximate to those required by a statistical tetranucleotide, but the purine/pyrimidine ratio varies among nucleic acids from different sources If the nucleases hydrolyse preferentially the pyrimidine nucleotide groupings and these are not distributed throughout the polynucleotide chain in any ordered sequence, it follows that the products of the enzymic degradation will vary in molecular size

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Research Correspondence

New Formulae for Double Refraction in Liquids

THE phenomenon of double refraction can be observed in isotropic substances subjected to strain Light polarized parallel to the direction of the strain traverses the medium with a velocity less than that of the light polarized perpendicular to that direction Double refraction occurs in isotropic liquids under application of an electric field (Kerr effect) or under the shearing action of viscous resistance forces in laminar flow It can be assumed therefore that molecules of liquids undergo a deformation, and the energy of the applied fields of forces is 'stored' in the form of potential strain energy of an electric nature

This assumption leads to a comparison between the magnitude of the increase of strain energy per molecule and that of the decrease of kinetic energy of light travelling through a material medium It has been found that the latter is equal to the former multiplied by the ratio of frequencies ν of light used in the experiment and ν of light absorbed by the medium Thus

$$E_{\text{total}} = E_{\text{potential}} + E_{\text{kinetic}} \qquad (1)$$

When E_{total} is constant

$$\Delta E_{\text{pot}} = -\Delta E_{\text{kin}} \qquad (2)$$

$$-\Delta E_{\text{kin}} = \Delta E_{\text{pot}} = \frac{\nu}{\nu_{\text{abs}}} E_{\text{strain}} = \frac{\lambda_{\text{abs}}}{\lambda} E_{\text{strain}} \qquad (3)$$

The term of the decrease of kinetic energy of light has been derived provisionally in the following manner

$$-\Delta F_{\text{kin}} = \frac{m(v-\Delta v)^2}{2} - \frac{mv^2}{2} = mv \times \Delta v$$
$$= -\frac{h\nu}{c^2} v\,\Delta v = \frac{h\nu\,\Delta n}{n^3} = \frac{hc\,\Delta n}{\lambda n^3} \qquad (4)$$

where m is the mass of the photon, c the velocity of light *in vacuo*, v the velocity of light in the liquid,

Δv the decrease of light velocity in the liquid as a result of the application of a field of forces, n the normal refractive index ($n = c/v$), Δn the increase of the refractive index when forces are applied ($\Delta n = c/\{(v - \Delta v) - c/v\}$), h is Planck's constant, ν and λ are frequency and wavelength of light *in vacuo* respectively ν_{abs} and λ_{abs} the frequency and wavelength of light absorbed by the liquid

The terms of the molecular strain energy have been derived as follows

a for viscous flow, strain occurs under the action of the viscous drag and viscous resistance on both sides of a molecule (both forces being equal) Therefore in order to obtain molecular strain energy the doubled drag term has to be multiplied by the volume occupied by one molecule

$$E_{\text{strain}} - 2\mu\left(\frac{du}{dy}\right) \times \frac{M}{\varrho N} \tag{5}$$

where μ is the absolute viscosity, (du/dy) the velocity gradient, M the molecular weight, ϱ the density and N is Avogadro's number

Hence

$$\frac{hc\,\Delta n}{\lambda n^2} = \frac{\lambda_{\text{abs}}}{\lambda}\, 2\mu\left(\frac{du}{dy}\right)\frac{M}{\varrho N} \tag{6}$$

$$\Delta n = \mu\left(\frac{du}{dy}\right)\frac{2n^2\,\lambda_{\text{abs}}\,M}{\varrho\, h c N} \tag{7}$$

Comparison with Maxwell's equation

$$\Delta n = \mu\left(\frac{du}{dy}\right) n\, K_M \tag{8}$$

gives the following term for Maxwell's constant

$$K_M = \frac{2n^2\,\lambda_{\text{abs}}\,M}{\varrho h c N} \tag{9}$$

in close agreement with values observed

	K_M *observed*	K_M *calculated*
Benzene[1]	0.91 × 10^{-10}	0.90 × 10^{-10}
Toluene[2]	1.04 × 10^{-10}	1.08 × 10^{-10}

b for an electric field the molecular strain energy has been calculated as a product of electric polarization and electric internal field strength divided by the doubled capacity The amount obtained has to be halved because the strain in the plane perpendicular to the light beam direction has no influence on the double refraction effect

$$E_{\text{strain}} = \frac{1}{2}\,\frac{(\epsilon - 1)\,E\left(\frac{\epsilon + 2}{3}\right)E}{8\pi} \times \frac{M}{\varrho N} \tag{10}$$

where ϵ is the dielectric constant and E the field strength in absolute units

Hence

$$\Delta n = E^2\,\frac{(\epsilon - 1)(\epsilon + 2)\,M\,n^2\,\lambda_{\text{abs}}}{48\,\pi\,\varrho\,h\,c\,N} \tag{11}$$

Comparison with the Kerr equation

$$\Delta n = \lambda E^2 K_E \tag{12}$$

gives the following term for Kerr constant

$$K_E = \frac{(\epsilon - 1)(\epsilon + 2)\,M\,n^2\,\lambda_{\text{abs}}}{48\,\pi\,\varrho\,h\,c\,N\,\lambda} \tag{13}$$

Benzene is that compound in which the whole strain seems to act in one direction only In the case of benzene therefore the best agreement of the calculated and observed values has been obtained

calculated $K_E = 0.43 \times 10^{-7}$

observed[3] $K_E = 0.408 \times 10^{-7}$

Deviations from the above equation are due to the inadequacy of Langevin's internal field strength formula in the case of dipoles and to the situation of bonds in molecules For example, compounds with tetrahedral symmetry give a very small double refraction effect and V-shaped compounds even a negative effect

It is impossible also to calculate accurately the third effect of double refraction in liquids—namely the Cotton-Mouton effect in a magnetic field—because in this case the mechanism of both paramagnetism and diamagnetism seems to promote double refraction, when on the other hand magnetic susceptibility is a resultant of the counteraction of both effects Thus the equation

$$\Delta n = \frac{\kappa B^2\,\lambda_{\text{abs}}\,n^2\,M}{2\,\varrho\,h\,c\,N} \tag{14}$$

(where κ is the susceptibility and B the magnetic fields strength) gives lower values than observed (benzene and toluene about 30 per cent difference)

Nevertheless in spite of these deviations study of energetic relations would seem to be of great importance, not only for double refraction but for the entire problem of the nature of light

A detailed account of the work will be published in the near future

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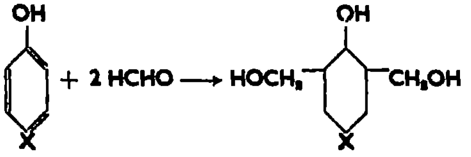
Shift of the Aromatic Band in Substituted Benzene

The aromatic band at 671 cm^{-1} for benzene shifts as a consequence of substitution in the ring, and for mono substitution the band is found at 740 to 760 cm^{-1}. The band for phenol is found at 750 cm^{-1}. In the case of *para* substituted phenols the band is largely unaffected by the molecular weight of the *para* substituent and appears at 825 to 830 cm^{-1}, and there is evidence that the *ortho* phenols with the band at 750 to 755 cm^{-1} are likewise substantially unaffected by the size of the *ortho* substituent.

Now it is well known that *para* substituted phenols can react with formaldehyde by addition to the carbons adjacent to the phenol group



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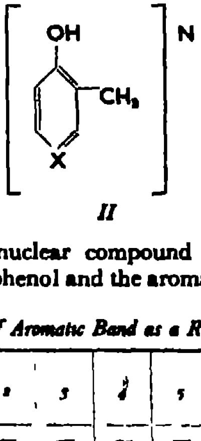
The aromatic band of such dialcohols we find at 870 to 880 cm^{-1} and appears independent of the size of X from methyl to octyl.

Furthermore, if the 2, 6 methylol substituted phenol is reacted under suitable conditions, poly nuclear substances of the type



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result. The dinuclear compound is a symmetrical 2,4 substituted phenol and the aromatic band appears at 813 cm^{-1} in the case where X is CH$_3$. The trinuclear compound, however, consists of a 2, 4, 6 substituted phenol between two 2, 4 substituted phenols and, as expected, there are two absorption bands the stronger band at 816 cm^{-1} being due to 2, 4 substitution in the phenol, and the weaker band at 870 to 880 cm^{-1} being caused by the central 2, 4, 6 substituted phenol. Substitution of the *para* substituent from methyl to octyl does not cause shift of these bands.

The shift of the aromatic band as a result of substitution in the phenol molecule is shown in *Table I*.

Table I *Shift of Aromatic Band as a Result of Substitution*

Position of substituent	*1*	*2*	*3*	*4*	*5*	*6*	*Aromatic band cm^{-1}* 671
	OH	—	—	—	—	—	750
	OH	X	—		—	—	750–755
	OH	X	—	—	—	X	760
	OH	X	X	—	—	—	770
	OH	—	X	—	—	—	780–785
	OH	X	—	—	X	—	800
	OH	X	—	X	—	—	813–818
	OH	—	—	X	—	—	825–830
	OH	—	X	—	X	—	830
	OH	X	X	—	X	—	840
	OH	X	—	X	X	—	835–865
	OH	X	—	X	—	X	870–880

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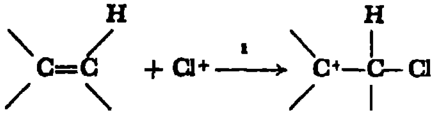
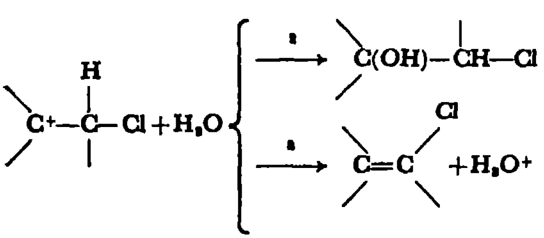
Reaction of Chlorine Cations with Olefins

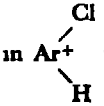
In the reactions of olefins with halogens and their derivatives (Hal—X e.g. Cl$_2$ or Cl—OH), the initiation process is generally regarded as the attack of a positively polarized halogen atom ($\mathrm{Hal}^{\delta+}$—$\mathrm{X}^{\delta-}$) on an unsaturated carbon centre of high electron density. The electrophilic activity of such reagents is assumed to depend on the degree of polarization of the molecule, which, in turn, is related to the electron attraction of X. The work described in a previous communication[1] prompted us to seek evidence of the formation, and the effectiveness in the reactions with olefins, of the most powerful electrophilic chlorinating agent possible, namely, the chlorine cation, Cl$^+$.

Using hypochlorous acid (*c* 0·002M) in the presence of perchloric acid (0·10M) and silver perchlorate at 25°C, we have observed reactions which are of the first order with respect to hypochlorous acid, are dependent, as to rate, on the acidity of the medium, and are of zeroth order with respect to the olefin. In the concentration range examined, namely, 0·001–0·004M, allyl ethyl ether, for example, undergoes reaction at a rate which is practically independent of its concentration and identical with that obtained under the same conditions for allyl fluoride (0·004M). Variation of the concentration of silver ions ([Ag$^+$] = 0·01–0·05M) did not appreciably change the rate. For these olefins, the first order rate coefficient, calculated from the rate equation, $v = k[\mathrm{HOCl}]$, with [H$^+$] constant (0·10M), has the approximate value 6·6 × 10^{-4} sec^{-1}. Moreover, practically the same rate (6·3 × 10^{-4} sec^{-1}) is observed for the chlorination under comparable experimental conditions of aromatic compounds such as anisole

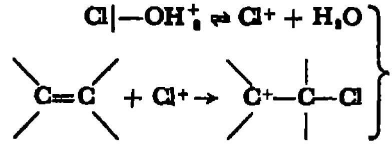
As in the similar case of aromatic chlorination, this result establishes the formation and effectiveness of the chlorine cation in the reactions with olefins under the conditions described The carbon cation formed in this interaction may give the chlorohydrin by reaction with water or it may suffer internal neutralization with loss of a proton to yield a substitution product of the olefin[2, 3] *e g*





Reactions 2 and 3 correspond to the second (fast) stages of unimolecular substitution and elimination, respectively, in saturated aliphatic structures, the heterolysis, R—X ⟶ R^{+} + X, constituting the first, rate controlling, stage in these processes In the case of aromatic halogenation, the reaction which corresponds to 2 is suppressed in favour of 3, doubtless owing to the great tendency, in  $\mathrm{Ar}^{+}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{H}\end{smallmatrix}$ to reach the resonance-stabilized aromatic structure[1], ArCl

Concerning the range of application of the first order mechanism, for which the rate is independent of the nature and concentration of the unsaturated substance, many olefins may satisfy the necessary condition that a sufficiently rapid removal of Cl^{+} should be effected However, a limitation of another type is observed This is imposed by the occurrence of a reaction in which the olefin may combine with another form of the reagent ($Cl—OH_2^{+}$ or Cl—OH) at a rate which may compete with, or predominate over, the rate of formation of Cl^{+} The most reactive olefins appear to prefer this route Regarding the olefin as a nucleophilic reagent towards hypochlorous acidium ion, it is tentatively suggested that the first order process and the second order mechanism now envisaged may bear the same relation to each other as do the unimolecular and bimolecular mechanisms of nucleophilic substitution reactions *e g*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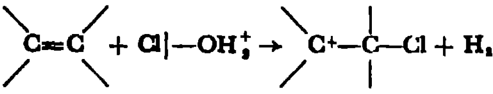
(2)

The most reactive aromatic compounds may also have a tendency to follow route 2 in favourable circumstances

We are greatly indebted to Professor C K Ingold, F R S, for inspiring discussions in the course of the studies described in this and the previous note

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Mechanism of the Weissenberg Effect

In a recent paper Oldroyd[1] has derived the rheological equation of state of an elastic liquid which shows the Weissenberg effect In a footnote he refers to two different views on the mechanism of this effect as expressed by Reiner[2] and by Rivlin[3] Reiner[2] and Rivlin[3] have shown that such an effect can arise in a non-newtonian viscous liquid exhibiting no elasticity, and Reiner[4] and Rivlin[5] have also shown that a non-hookean elastic solid exhibiting no viscous flow could manifest an analogous effect of extending in a direction normal to the direction of shear Rivlin[5] has demonstrated the latter effect experimentally by means of the torsion of a rubber cylinder where normal pressures must be exerted over the plane ends of the cylinder in order to hold it in a state of simple torsional deformation It may be mentioned that this latter phenomenon was observed before by Poynting[6] on steel wires In accordance with these theoretical considerations the Weissenberg effect in an elastic liquid could be attributed to either the elasticity or the viscosity of the material alone, and no theoretical criterion was available to decide between both

We have now made experiments with rubber-toluene solutions of from 7 to 12 per cent concentration in which the material is sheared between a rotating lower and a stationary upper disk, the upper one opening at its centre into a tube The tube, fixed to the upper disk, is suspended by a torsion wire which measures the viscous resistance When the lower disk is rotated the liquid rises in the tube to a maximum which depends upon the velocity of rotation and the concentration, but after a while falls off to zero height When the liquid is given a rest it regains the Weissenberg effect, the amount depending upon the time of rest However all the time the twist of the suspension wire remains the same, which means that the viscosity of the liquid is not changed and is the same for the state in which the Weissenberg effect is present and the one in which it is absent We are continuing our investigation into the causes of this, so to speak, elastic thixotropy, but the fact that the viscosity is not affected seems to us to prove that the Weissenberg effect is, at least in the case of a rubber-toluene solution, not connected with the viscosity of the liquid

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Improved Method for Precipitation of Polymers from Solution

In the course of work done in this laboratory on the preparation of acenaphthylene polymers we have had occasion to examine many samples by the precipitation method

This consists of adding a 2 per cent benzene solution of the polymer to alcohol in the ratio of 1 of benzene to 3 or 4 of alcohol If smaller ratios of alcohol are used the precipitate comes down in a sticky, gummy form from which it is difficult to free the polymer of solvent and monomer This method involves the use of large quantities of alcohol which cannot be recovered easily since it forms an azeotropic mixture with benzene Further, drying to constant weight takes anything up to 24 hr or even longer.

In view of these disadvantages which we and others [Lewis and Mayo *Ind Eng Chem.* 17 (1945) 134] have experienced an attempt was made to improve the method

'Dry ice' is added to the alcohol and this is allowed to cool to about − 40°C before addition of the polymer solution, whereby a ratio of 2 : 1 alcohol-benzene is found to be adequate for the precipitation of the polymer in a light, fluffy form This can be washed easily and completely, provided that care is taken to carry out the washing with cold alcohol The use of room temperature alcohol causes the reversion of the precipitate to the gummy form

The effect of solid carbon dioxide is mainly due to cooling but it is noticeable that the bubbling in alcohol helps to break up the precipitate as it is formed For this reason as well as for ease of working we prefer to have the coolant in the liquid rather than surrounding it

This small modification brings about three advantages *1* it gives the polymer in a form which is washable, *2* it reduces the drying time to about 3 hr at about 75°C, *3* it makes possible a considerable economy in the use of alcohol

I would like to thank the Directors of the Company for permission to publish this note

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Commentary: Progress in Manual and Automatic Control Apparatus

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THE RECENT ESTABLISHMENT by the Society of Instrument Technology of a distinct section to be concerned with manual and automatic controls is a significant and useful development It is to be hoped that these activities will be a useful supplement to those of such senior bodies as the Institution of Electrical Engineers and the Institution of Mechanical Engineers, which have already shown their appreciation of the need to encourage progress in this field Automatic control is a branch of engineering which is in a phase of rapid development and new achievement The stimulus came in the first place from problems encountered during the war, and it is being maintained by the demands of industry for the saving of man-power and for increase in the speed and quality of production

During the war many outstanding new examples of precision automatic control were devised It became possible for example to lay guns automatically, on the deck of a rolling ship, to the angles indicated by an automatic computer, with errors never exceeding a few minutes of arc and where power outputs of tens or even hundreds of horse-power were involved Another example is the automatic pilot, which will hold an aircraft on a pre-set course and operate rudder, elevator and ailerons with a precision which cannot be equalled by a human pilot Automatic tracking of aircraft from the ground by radar was developed, and there were many similar wartime innovations

These developments were accompanied by new attempts to clarify the principles underlying all control systems The problems were not entirely new, for similar problems had been solved early in the century in such fields as the design of automatic engine governors and voltage regulators, but new methods and types of mathematical analysis, which have been made familiar to engineers in the problems of telecommunications, have recently been brought to bear on control problems with most fruitful results

It is natural that engineers concerned with industry should have been stimulated by these developments to a fresh examination of the field for the use of automatic controls, and the improvement of manual controls, over the whole range of industrial needs, from precision measurement to operations like the rolling of steel strip involving thousands of horse-power Much progress has been made, and many new applications are in process of development and practical trial The present economic position, with increasing certainty of large and well sustained demand, the need for economy in man-power, and the need for maintaining uniform high quality of output, presents a challenge, to meet which the industrial engineer must explore and judiciously apply the possibilities which wartime developments have opened up

The problems of manual and of automatic control are similar Consider the simplest kind of control operation, for example, a human operator required to maintain the temperature of a vat constant by operation of a valve controlling the supply of heat to it The operator is provided with a measuring instrument, here an instrument indicating temperature, and his task is so to operate the valve as to maintain the reading of this instrument constant at a particular mark on the dial. The movements which he gives to the valve are determined by the amount by which the pointer deviates from the mark, and its rate of movement.

In any such situation in which a human operator makes some movement or adjustment, depending, in accordance with any predetermined rule or schedule, on the readings of an instrument, it is possible to make a mechanism —a robot—which will act within this limited stereotyped pattern of response in the same way as the human operator, but the robot may be more sensitive, more rapid and more powerful than a human being.

Such controls, whether they are manual or automatic, are essentially 'closed sequence controls'. In the example mentioned a movement of the pointer from the mark results in a manual or automatic movement of the valve, which again results in a movement of the pointer, so that there is a closed sequence of the successive dependence of one quantity on another.

The chief advance in the understanding of such systems and their limitations has been the recognition that the accuracy of control that can be achieved in any closed sequence system is limited in accordance with the time delays which exist in the response of the various quantities, one on another, which form the closed sequence. The enemy of continuous close control is time delay. Superlative performance can be achieved if time delays can be sufficiently reduced. An attempt to increase the accuracy of control beyond the limit set by the speed of response will commonly result in an unstable system and the phenomenon of self sustained oscillation, which the engineer has long known as 'hunting'.

The human operator, as an element in a control system, is particularly handicapped by the time delay which occurs between his perception of any event (such as the movement of the instrument pointer) and the muscular movement which he may make as a result (such as an operation of the valve handle). This delay is about 0.3 second. An electric motor controlled from a photoelectric cell might perform the function in 0.01 second or less. The time delay of response of a human operator is not a matter which can be corrected by increase of skill. It is due to the low speed of the electrochemical pulses which constitute messages transmitted along his nerves, and the delay at the transfer, in the central nerve organs, of the message from the incoming to the appropriate outgoing nerve fibres. It is unlikely that this basic time delay can be reduced, and this constitutes a fundamental limitation in the performance of any control system which involves a human operator as an element. This is one reason, among others, why mechanical devices can often surpass human operators in performance.

In mechanical robots time delays can be reduced, but where large amounts of power have to be handled they cannot at present be eliminated. These time delays are due to energy having to be stored in the system in order that power may be developed by it. The ratio of energy stored to power output is a 'time constant' of delay.

Progress in control systems involving large powers has recently been made by the invention of the various types of multi-stage direct current electric generators, the metadyne, the amplidyne, the rototrol, the magnavolt and others. All of these have the same fundamental principle. They are DC generators in which multiple use is made of the same armature, using various combinations of poles to produce the field, and so providing, in a single machine, much the same effect as could be obtained by a multiplicity of separate generators, each exciting the next in cascade. These new types of generator may be arranged to give a specified power amplification with a far more rapid response than is possible with the ordinary single stage generator. Many other new elements and devices have been made available, mostly as a result of wartime development, which may now be made the basis of new industrial progress.

SCOPE FOR FURTHER DEVELOPMENT IN CONTROL SYSTEMS

It is an appropriate moment, as a new body is coming into existence for the purpose of accelerating progress in this field, to assess the present state of development of control devices and control theory, and to attempt to discover what investigations and developments seem to be most likely to lead to valuable industrial results The industrial operations and processes that seem to offer some possibility of economical application of continuous automatic error-actuated controls—as distinct from mere automatic sequencing and the like—are not so numerous as might perhaps be expected

Taking the steel industry as an example there are obvious needs for continuous automatic control of some degree of precision in such cases as the control of furnace temperatures and ingot cooling rates, the currents in arc furnaces, the thickness of rolled strip and plate, the tension in reeling, and a number of similar problems

There is also the larger field of what may be called 'manipulation', the moving, turning over and positioning at high speeds of masses of hot metal This is a more difficult field There are of course some operations, such as the location of the edge of a moving strip, which invite the application of 'an electric eye', but it seems unlikely that the human operator will be eliminated from the processes of ingot manipulation and the like The relevance of recent control developments in this case is the clearer understanding which is emerging of the nature of a human operator's skill, and sources of his limitations, which makes possible the design of controllers of such characteristics as will facilitate the acquiring of skill and make faster operation possible Experimental work that originated in attempts to improve the manual laying of guns on targets and which is being continued on a broader basis may provide a basis for future improvements in such fields

It would be easy to make an equally impressive list of potential applications of automatic control for other industries In the chemical and oil industries the possibilities are particularly extensive, for at every point the quality of product demands the continuous and rapid regulation of temperatures, flows, pressures, gaseous mixtures, acidity, and other quantities Such 'process control' has advanced further in the U S A than in this country, in the production of petrol, ammonia, nylon and so on The latest developments are in the direction of control of the plant processes as a single entity, using complicated computing devices, part of the data sometimes being fed in from the output of an automatically operated mass spectrograph continuously and instantly checking the quality of the final product, and instigating the adjustments necessary to maintain the required quality.

REQUIREMENTS FOR MORE RAPID PROGRESS

Extension of the applications of automatic control is taking place more slowly than might be expected in view of what is now technically possible This is largely due to the high cost and the often unnecessary elaboration of automatic equipment The prospective difficulties of maintenance of intricate apparatus as well as its initial cost is a deterrent to its use

Simplification and cheapening will be assisted by a clearer and more wide-spread understanding of the principles of control system operation, and by the development of better methods of design for specific or optimum performance

The theory of control systems is a fascinating field which links up with communication theory and with the theory of electrical networks and filters, and which (so long as the relations involved are linear) permits the use of mathematical methods of great generality There is no doubt that valuable practical results are to be expected from developments of a theoretical kind The analysis of the behaviour of a given system is not difficult, but the problems of synthesis—the selection and combination of elements which will meet given requirements in an optimum way—have not yet been solved. When they have been solved it will probably be found that many elaborations and ingenious but arbitrary variations disappear in favour of simpler and relatively standardized elements and combinations

There is scope in this field for the combined efforts of mathematicians, designers of electrical and pneumatic apparatus, inventors, physiologists and psychologists and it is to be hoped that the new section of the Society of Instrument Technology will be successful in its aim to provide a common meeting ground for all such contributions

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Grafting

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THE origin of the practice of transplanting plant parts is lost in antiquity The Chinese, and the Greeks, were quite familiar with the process and have left evidence that the technique was commonly employed Whilst some of the ancient writers seem to have had peculiar notions as to the uses of grafting it should be remembered that those most skilled in the art were not the most likely to record their ideas in writing Scholarship was not commonly an attribute of husbandmen

Since our most venerable archives treat grafting with some familiarity it is evident that its origin was considerably further back Moreover, its use by widely separated civilizations leads one to suppose that it arose from observation of plants in their natural state, much as the processes of seedsowing and division were copied from nature Natural grafts are commonly found in woodlands and hedges, where the branches are congested Beech *Fagus sylvatica* provides numerous examples and many others have been recorded[1] The common climbing ivy *Hedera helix* is a very ready source of natural grafts and frequently has to depend on these unions for its existence Thus it comes about that the cutting of almost all connection with the roots incommodes climbing ivy very little M E MILLNER[2] made a study of natural grafting in this plant and showed that the establishment of grafts depends largely upon firm anchorage of one stem upon another

Natural grafts commonly occur between the roots of trees but are less frequently seen because of the almost negligible opportunities M LUSCEN[3] observed that a cluster of trees may be so thoroughly joined that all the roots will survive after all but one tree has been cut through at ground level

NATURAL GRAFTS

Close examination of plant parts in contact shows that a rind rupture has occurred and the healing of wounds in contact with each other has effected a junction In fact, grafting is the healing in common of two or more wounds, and for this to occur the wounds must be firmly anchored in relation to each other Thus the two essentials for success in grafting may be learnt by observation of natural grafts and it seems reasonable to suppose that artificial grafting followed and took similar form to those methods commonly known as ' grafting by approach ' Grafting with detached scions must surely have been a later invention probably encouraged by observation of damaged approach grafts The best formed natural grafts are found to occur between stems or roots which lie in the same direction Inversion of complete rings of rind around a stem causes not only the death of the ring but also that of the stem above It is therefore vitally important to observe an ordered polarity in the components

CAMBIAL CONTACT

It is usually considered that contact between cambia is essential for successful grafting this has to occur of course but mutually adjacent tissues are also involved Wound healing callus is generally produced by tissues lying outside the xylem, any of which except the cork may be involved It is also seen to arise from the medullary rays and in the pith region Callus production is initiated by cells that have remained meristematic but may in some cases be followed by a resumption of the meristematic state by adjacent differentiated tissues

K MENDEL[4], who made a detailed examination of union formation in bud grafted citrus, found that in the operation of raising the rind of the rootstock (*i e* the root bearing plant on which the scion is grafted) the separation usually occurred in the secondary bark and in the cambium, but sometimes partly in the youngest sap wood The removal of the bud shield from the scion wood usually involved separation in the secondary bark or in the cambium New cells were observed at the wound surfaces between 24 and 48 hours after the operation, callus formation being most active on the rootstock wound, less on the raised bark flaps, and slowest on the bud shield The cavities between the bud shield and the rootstock, and beneath the flaps of rind raised from the rootstock, are gradually filled with callus, *Figure 1* The callus masses meet, and by a union of the cells, form one gapless tissue Where the wounded surfaces of the components lie in intimate contact, as at or near the edges of the bud shield, no callus is formed and the tissues grow together directly The primary callus, filling the gaps, is transformed through differentiation into permanent tissue and the whole union process is uniform and continuous

The characteristic continuous cambium and related elements in the dicotyledons lend themselves to the grafting process On the other hand, the scattered arrangement of the vascular bundles in the monocotyledons and the absence of secondary thickening involve difficulties for the grafter Thus, however, has not always deterred investigators Virus diseases have been transmitted[5] from one liliaceous plant to another across a graft union The grafting of tulips and related subjects is commonly achieved at the Bulb Research Station at Lisse in Holland

Extensive use has been made of grafting in the so-called hybridization of cereals in Russia[6] using both approach and detached-scion grafts in the nodal region of young plants

COMPATIBILITY

Once intimate contact is established between meristematic tissues grafting may occur, but for a permanent and healthy union compatibility between the components is essential This is so well known that no one seriously sets out to unite a member of one botanical family with that of another Even so, the botanist's classification serves only as a rough guide for it is founded mainly upon the floral structure and the grafter essays to join the vegetative organs In fact, as W H CHANDLER[7] writes something more than kinship is required for a sound union

In spite of extensive research into the causes and manifestations of incompatibility between plants when grafted there is, as yet, no clear answer to the problem and each combination must be tested for its compatibility An example of the complexity has been observed when grafting plum rootstocks with peach scions Four seedling plums *Prunus domestica* were selected, multiplied vegetatively, and bud-grafted with one variety of peach Selections 1 and 2 formed perfectly compatible unions, though differing in vigour, selection 3 made vigorous young trees, all of which died before they were five years old, whilst selection 4 failed to survive beyond the first year Yet the same variety of peach is compatible with selected *P domestica*, *P insititia*, *P cerasifera*, *P armeniaca* and *P Besseyi*, the last being a species of cherry

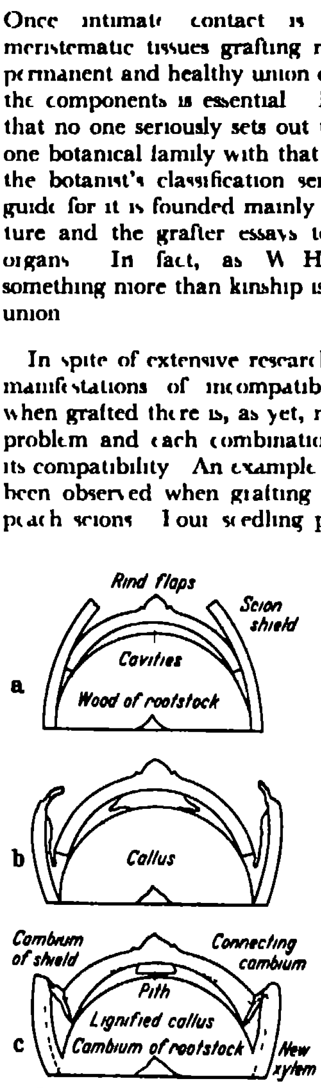

Figure 1 Diagrammatic cross section of a bud graft (after K Mendel), a when first grafted, b after ten days, c union complete

Figure 2 A well grown pear tree broken cleanly from a quince rootstock with which it is incompatible

Incompatibility can take many forms and it is clear that factors other than this may produce very similar effects G K ARGLES[8] suggests that the term ' incompatible ' should be reserved for distinct failure to unite in a mechanically strong union, failure to grow in a healthy manner, or premature death, where such failure can be attributed with a reasonable degree of certainty to differences between stock and scion

One of the most striking forms of incompatibility is breakage at the union, *Figure 2*, where the fibres of scion and rootstock fail to interlock This incompatibility has been overcome[9] by the use of an intermediate stem piece or bridge of a variety compatible with both scion and rootstock The use of an intermediary severally compatible with rootstock and scion is not invariably successful, for the plum President, which is compatible with the plum rootstock Myrobalan B, when top-grafted with the plum Victoria, itself compatible with Myrobalan B, becomes incompatible at the President/Myrobalan B junction[10]

Equal growth rates and cycles have been regarded by W T CHANG[11] as essential accompaniments to a congenial graft union, based on normal behaviour of the non-grafted plant However, there are many congenial combinations which show growth differences and, conversely, failures between plants of similar habits Moreover, as R J GARNER and D H HAMMOND[12] showed, the time of the operation in relation to season neither delays nor hastens the onset of incompatibility symptoms

Differences in vigour of stock and scion do not necessarily result in tree failure as is clearly shown by the healthy alliance of vigorous and dwarfing varieties *e g* the triploid apple Bramley's Seedling with the weaker growing apple rootstocks, and the weak growing damsons *P insititia* with the vigorous Myrobalan plum *P cerasifera*

Biochemical studies have not so far revealed any basic chemical causes of incompatibility F C BRADFORD and B G SITTON[13] studied the histological differences between stock and scion and suggested that uncongenial unions may be due to differences in the size of cambial cells H J TOXOPEUS[14], working with citrus, suggested that the scion produced some substance toxic to the stock In the last decade considerable attention has been paid to 'quick decline' diseases of citrus and the cause attributed to something of a virus nature[15] Such a virus may be present in a variety and may become manifest when united with another by means of grafting Certain incompatibilities in apples and cherries may have a similar origin

COMMERCIAL APPLICATION OF GRAFTING

Vegetative transplantation, whether it be by cuttings or layers into a soil or, as in grafting, into a plant with which it is compatible, serves to perpetuate the characters of the original plant Thus the chief use of grafting is for the vegetative multiplication of selected varieties especially where propagation by cuttings or layers is inefficient or inconvenient The comparative ease with which two related plants may be intergrafted has encouraged the use of grafting in the multiplication of any plant which normally proves difficult by other means This has naturally led to the use of rootstocks the chief attribute of which is their ready availability The fact that scions are usually united with other varieties involves the production of a composite plant and R G HATTON[16] established that a large measure of control can be exercised over growth and cropping by the use of selected rootstocks

For the fruit industry, Hatton's painstaking study of the mutual influence of rootstock and scion has proved, and is proving, invaluable Hatton demonstrated the uniformity achieved by the use of vegetatively propagated material and was able to predict the behaviour of various rootstock/scion combinations under given conditions, which has since led to the efficient production of fruit in situations where, hitherto, it had proved quite unremunerative

Whilst in general the scion is married to the rootstock in the nursery in the simplest possible way, either by bud grafting (budding) or splice grafting with dormant scions, grafting is most fully developed when applied to established trees in the plantation and orchard The grafting of mature fruit trees becomes necessary when conditions engender a desire to change from one variety to another This regrafting, or reworking as it is commonly termed, is done in two main ways, either by topworking or by frameworking, *Figure 3*

Topworking— In topworking, much of the main branch system of the tree is removed and scions are inserted in the cut ends of the main limbs, usually within two or three feet of the crutch Small branches below the general level of grafts should be left intact for a time in order to feed the roots until the ingrafted shoots have grown out sufficiently Branches left temporarily are known as 'sap drawers', the presence of large sap drawers' in no way diminishes scion growth but, on the contrary, increases it and reduces the risk of loss due to post-grafting diseases such as papery bark canker[17]

Frameworking— In frameworking, the main branch framework of the tree is entirely retained and furnished with scions for the production of fruiting laterals and extension branches The initial cost of frameworking is much higher than that of topworking, but there are some important advantages Frameworked trees remain healthy in situations where topworked trees die from diseases such as silverleaf and papery bark canker[18, 19] The number of scions inserted on a single mature tree may vary according to local custom but up to a thousand scions have been used on very large apple trees The number of operations involved in such processes calls for a simplified technique

Outstanding amongst the methods used is the stub graft in which the scion base is cut to form a wedge which is inserted into a cleft at the base of a lateral on the framework of the tree This cleft is formed by a single cut, opened by bending the lateral, into which the scion is inserted and held when the lateral is released The lateral is then severed above the insertion

CONSTRUCTION OF RESISTANT PLANTS

Variation in degree of resistance to adverse conditions, or to diseases of various kinds, is a common phenomenon in plants, of which practical use is made The winter frost resistant apple Antonowka has been used with success by W FILEWICZ[20] in the construction of trees capable of withstanding the severe winters experienced in Poland The hardy Antonowka is used for the stem and lower parts of the main limbs which are later grafted with the tender fruitful variety It was found that the retention of one or two small limbs of the Antonowka on the

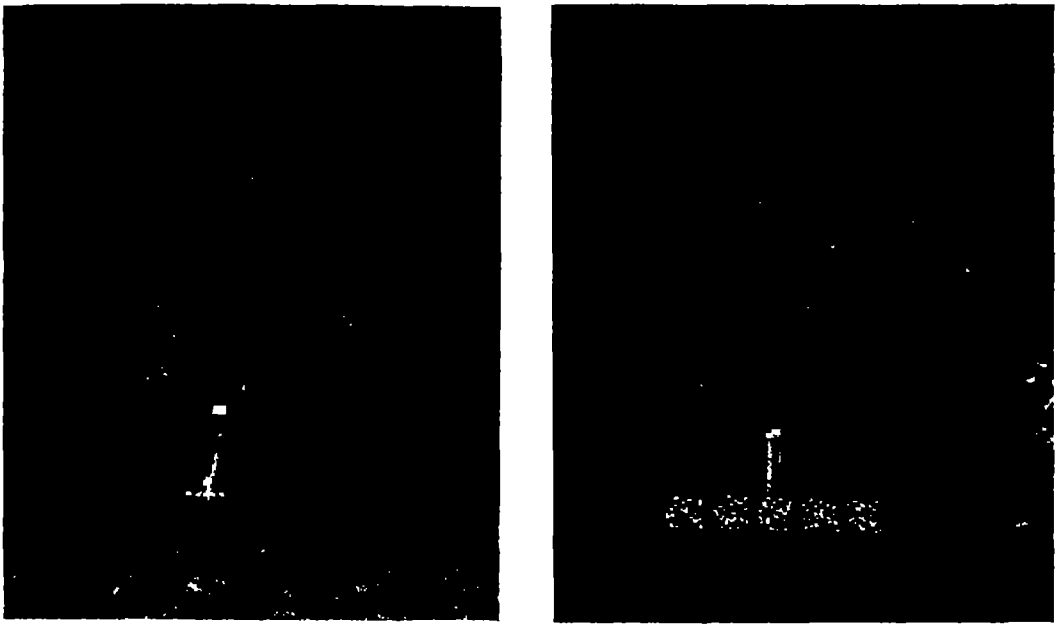

Figure 3 Similar apple trees, a *topworked and* b *frameworked Photographed three seasons after grafting*

south west side of the tree made the scion above more resistant

Where otherwise desirable varieties are susceptible to attack by soil fungi it is possible to use a disease resistant stock, as is now fairly common practice with cucumbers in Holland, the cucumber being grafted on to the collar rot resistant *C ficifolia* H B S MONTGOMERY and others[10] report that plum trees in England have been made more resistant to 'Bacterial Canker' *Pseudomonas mors-prunorum* by constructing the trunk and main limbs of varieties resistant to the disease The ravages of the 'Woolly Aphid' *Eriosoma lanigerum* of the apple have been checked by the use of rootstocks highly resistant to the pest, the Northern Spy rootstock, which suffers no damage from the pest, has been used with considerable success in Australia and New Zealand and, to some extent, in South Africa[11]

TREE SURGERY

If the rules of cambial contact and polarity and, of course, relationship are observed, there seems to be little limit to the use of tree surgery When trees have been completely girdled by animals or other agencies they die, unless branches and roots are suitably reconnected

In large trees death may not occur till one or two years later but it is inevitable first in the roots, then in the branches A very simple technique for treatment is adequate, yearling shoots are used to connect the undamaged parts and these quickly increase in size and before long take over the functions of the stem or trunk

This has recently been used with success in the bridging of incompatible unions between pear and quince in commercial plantations This bridging of incompatible unions has also been accomplished merely by the insertion of panels of rind of a mutually compatible variety, across the union Such panels are known to extend sectorially and 'staple' the original scion

J HEARMAN and others[12] invigorated weakly growing trees by inarching into them their more vigorous relatives When first done this operation invigorated only those parts of the plant which were in direct vascular connection with the vigorous component but later the influence spread through the tree The early effect of this influence is hastened by inserting the plant inducing vigour in line with the divisions of the main branches so achieving immediate contact with the vascular systems of more than one branch In apple trees the beneficial effect of vigorous inarches has been noticeable within three years, and thereafter the growth and health of trees previously stunted have greatly improved W H CHANDLER[13] reports that pear trees in America which bore black-end fruits, because they were worked on *Pyrus pyrifolia*, were cured by inarching with *P communis* The trees continued to bear black-end fruits until the inarched plants had replaced the functions of the *P pyrifolia* roots and these had been cut away

GRAFTING IN BIOLOGICAL RESEARCH

In the extensive studies of the relationship of rootstock and scion, with which R G **HATTON** will always be associated, grafting was indispensable Whilst in most of this work the trees were composed of two individuals joined by a single graft there were occasions when numbers of rootstocks and scions were amalgamated in complex systems with a view to resolving some of the particular difficulties of biological research

All plant viruses are transmitted by grafting and much use is now made of grafting to investigate the health of plants, to map symptoms and to amalgamate viruses for research purposes For such transmission 'organic union' is generally vital but it does not follow that a successful and lasting union is necessary, since the incompatible union is no barrier to virus transmission In the selection of healthy colonies of strawberries *Fragaria* spp considerable use has been made of stolon grafting by R V **HARRIS** and M F **KING**[4] The stolons survive only one season but efficient transmission occurs directly a union is established

Special use has been made of the bottle graft technique, *Figure 4*, for virus transmission by C H **CADMAN**[5] A growing shoot is collected, preferably by severing under water, and placed in a bottle of water in which it stays whilst it is approach grafted to an established plant, the bottle remaining until a union is effected

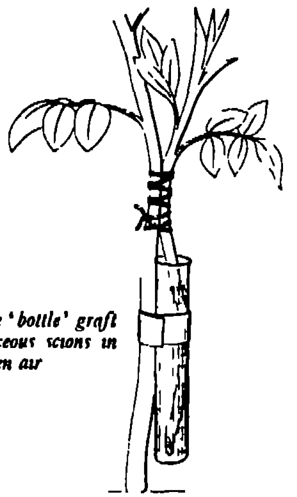

Figure 4 The 'bottle' graft used for herbaceous scions in the open air

Though grafting in commerce is confined to perennial plants, annual plants are equally susceptible to this technique, in fact the rapidly growing tissues associated with shortlived plants appear to graft far more readily than those of the majority of woody subjects The virus of the 'woodiness' disease of passion fruit *Passiflora edulis* has been transmitted by single leaf grafts[6] Actually a junction is formed between the petiole and the cortical tissues of the stem and it does not matter whether or not the dorsal surface is uppermost

J M **WALLACE**[7] has used leaf tissue scions to transmit virus diseases in citrus and prunus The process is intriguingly simple Small pieces of lamina were placed beneath raised strips of rind Examination of leaf pieces some thirty months after insertion revealed that they were not only living but still possessed chlorophyll, although buried, by then, beneath three to four millimetres of xylem Union occurred only at the cut edges of the leaf pieces and at any small incidental wounds which had occurred during the operation This was clearly demonstrated on floating sections

Grafting is also employed in plant hormone studies Research into vegetative propagation by cuttings is making increasing use of grafting to join, temporarily, ready rooting to shy rooting subjects The suggestion is that rooting stimuli are transferred, similar transference of the 'floral stimulus' has already been claimed K C **HAMNER** and J **BONNER**[8] using cocklebur *Xanthium pennsylvanicum* placed a layer of lens paper between the cut surfaces of the components, one of which was subjected to a long, and the other to a short, photo period It was found that the floral initiation stimulus was able to diffuse across the junction and it was considered that this demonstrated that a substance or substances were concerned However, A P and R B **WITHROW**[9] found that it was necessary to establish tissue union for at least four days Synthetic growth substances have been used[10, 11] to increase the rate of callusing and so the formation of the union, particularly when cutting grafting vines *V vinifera*, but stimulation of callus growth was always accompanied by an inconvenient amount of rooting in the region of the union

GRAFT HYBRIDS AND SPECIFIC INFLUENCE

H **WINKLER**[12] made a very full study of so-called graft hybrids, considering them under three heads

1 those due to specific influence
2 periclinal, sectorial, and mixed chimaeras
3 cell fusion graft hybrids

Specific influence defined as 'a permanent change in one component brought about by association with another, and such changed form transmissible by vegetative propagation' has not yet been satisfactorily proved to be other than temporary nutritive influence Chimaeras are fairly common and can be made by manipulation of graft unions as explained by C A Jorgensen and M B Crane[33] Chimaeras may also arise spontaneously as, for example, in the formation of the Golden Wonder potato which was found[34] to be a periclinal chimaera with an inner core of the variety Langworthy Cell fusion hybrids arising as a direct result of grafting have not been proved to exist In view of these definite statements the claims of I V Michurin's followers in the U S S R are of considerable interest T D Lysenko[35] reports that Michurin used methods to obtain vegetative hybrids in 'large quantities' A possible explanation is that these vegetative hybrids are not the chimaeras of Winkler nor cell fusion hybrids but rather plants which have been 'specifically influenced' An example of the Michurin method is much as follows Scions of an old established variety of fruit are grafted on a young seedling and this young seedling then acquires properties which it previously lacked, these properties having been transmitted from the old strain Michurin termed this old strain the 'mentor' and he used both rootstock and scion mentors at will and believed he had improved a number of new strains The Russian work claims to have shown that 'when an old established kind of heredity is being eliminated we do not at once get a fully established, solidified new heredity In the vast majority of cases what we get is an organism with a plastic nature, which Michurin called "shaken" ' These 'shaken' natures have a tendency to show some adaptability

The work of this group of Soviet biologists, like that of the French botanist Daniel, has received considerable attention but little support in scientific circles outside Russia In America K S Wilson and C L Withner[36] grafted together red, yellow, white, 'plum' and 'pear' tomatoes All combinations of defoliated stock or scion and defruited stock or scion, and controls were tried, and vitamin production in various parts was carefully analysed No evidence was obtained that differences between two graft symbionts in vitamin production were transferred from one component to the other, no changes in visible characters occurred, nor was time of fruit ripening changed

If 'specific influence' was of common occurrence one might not be surprised to find that the common fruit varieties in our orchards would have been 'shaken', at least when first produced, by grafting them upon old established rootstocks in the nursery or upon mature trees in the orchard Such 'shaken' heredities should then have acquired properties of the strains to which they were grafted Consequently we should expect to find a collection of differing fruits under one name It is well known that there are certain differences within a fruit variety but these are few and are traceable either to systemic disease or, much more rarely, to mutations, and in general the characters of our fruit varieties have been perpetuated for many centuries, without apparent change by repeated vegetative propagation Recent publication, in English, of I V Michurin's[37] original papers facilitates examination of his claims which, at least in some respects, fall short of those made on his behalf

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Industrial Filtration

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FILTRATION is a process in which a heterogeneous system consisting of a solid substance and a fluid is separated into its constituents, using a porous medium which retains the solid, but allows passage of the fluid The pressure difference necessary to force the liquid through the porous medium and through the layers of solid substance formed on this medium may be supplied by gravity alone, by using vacuum, by using fluid pressure (pumps or other means) or by centrifugal force The method will depend upon the quantities and properties of the system to be separated, the resistance to flow, the filtering area and the filtration time available The aim is to make this filtration time as short as possible, consistent with good separation and low cost

The porous media used in industry vary widely Examples are sands, coke, charcoal, earths, porous stones, sintered glass, perforated or slotted plates, metallic cloths, woven and unwoven cotton, silk, wool rayon, nylon, glass fibres and porous hard and soft rubber sheets

Filtration is one of the most important of industrial operations and much practical experience has been obtained Moreover great attention has been given to the theoretical side of filtration Despite this fact there is still a considerable gap between practice and theory The reason for this is that, although not obvious at first sight, the filtration process is complicated This implies that generally in practice the data necessary to design filtering machinery are not known or the desired conditions are not reached

In this review a discussion of present theoretical knowledge on filtration will be given, substantiating the view expressed above It should be noted that most of the work has been done on suspensions

THEORY OF FILTRATION

One of the simplest examples of industrial filtration is that of filtering water for drinking purposes This can be treated as the problem of liquid flow through a porous medium, neglecting the influence of the solid substance over short periods, and an expression can be derived for the rate of streamline flow through a porous medium[1]

$$\frac{1}{A}\,\frac{dV}{d\theta} = \frac{1}{A}\,\frac{V}{\theta} = K\,\frac{1}{\mu}\,\frac{\Delta P}{L} \tag{1}$$

where A is the filtering area, θ the time of filtration, V the filtrate volume, K the permeability of porous medium, μ the viscosity of fluid, L the thickness of cake layer, and ΔP the pressure difference over filter medium and cake Equation 1 is analogous to the equation of Darcy[1] for the flow of water through fine sands The viscosity term has been introduced in analogy with the Poiseuille-Hagen conception of streamline capillary flow The permeability K, which can be expressed in terms of the properties of the porous medium such as porosity, see p 257, is however not constant even for one system *e g* it is a function[2] of $\Delta P/I$ This function cannot be expressed mathematically, as the physical picture of flow is far from clear because of the complexity of the problem, even for a bed of spheres of equal diameters[3-6] Lack of insight into the physical details of the filtration process has hindered and still hinders the progress of filtration theory

Based on the same Poiseuille-Hagen conception of flow, for a sludge filtration during which a cake of increasing thickness is formed, the rate of filtration after a volume V has been filtered in the time θ, provided cakes of equal thickness are formed, can be expressed by

$$\frac{1}{A}\,\frac{dV}{d\theta} = \frac{1}{\mu}\,\frac{\Delta P}{R} \tag{2}$$

The symbol R represents the combined resistance per unit of surface, of cake and filtering medium It has been proved by several authors[6-9] that for most filtrations the introduction of the viscosity term is correct

For those filtrations in which the cake is formed over the porous medium the resistance term R can be split up into two components, R_k (cake resistance per unit of surface) and R_f (resistance of the porous medium per unit of surface) Therefore according to D R SPERRY[10]

$$\frac{1}{A}\,\frac{dV}{d\theta} = \frac{1}{\mu}\,\frac{\Delta P}{R_k + R_f} \tag{3}$$

To find the desired relation between V and θ, equation 3 must be integrated, hence the dependence of R_k and R_f on the filtration variables must be known

THE CAKE RESISTANCE

Introducing a specific resistance on a weight basis, following the suggestions of H I WATERMAN[7] and co-workers[11,12], expressed as the resistance of a cake of unit weight per unit of filtering area and observing that this resistance in general is not constant for the whole cake[14], a point resistance called the differential specific resistance r_d must be introduced

$$dR_K = r_d\, d\left(\frac{cV}{A}\right) \qquad (4)$$

where r_d is a function of a deforming force in the cake (which is equal to the pressure loss p in fluid in the cake[8]), c is the concentration of the suspension (weight per volume) and ΔP the pressure difference over filter medium and cake for one filter medium[15, 16] Contrary to P C CARMAN's opinion the deforming force is the actual pressure of solid on solid in the cake (A L BLOOMFIELD[17])

INCOMPRESSIBLE SLUDGES

For incompressible sludges, by definition, r_d is not a function of p and is therefore constant for the whole cake, and equals r_K, r_K is the constant specific resistance of a cake per unit weight per unit of surface However r_K is a function of the concentration c of the suspension Although this influence is felt only over a short concentration range at very low concentrations, it is a marked one, giving an increase of the resistance at lower concentrations It may be noted that J W HINCHLEY, S G M URE and B W CLARKE[18] and H PALL[19] found an increase in porosity with increasing concentration Further, r_K is a function of the initial velocity of filtration, r_K increasing at higher velocity In both instances r_K soon becomes constant In all probability the cause of both the observed phenomena is the same The structure of the cake formed by the first solid particles arriving at the filter cloth is determined by concentration and by the initial velocity of flow Moreover, apparently the first layers determine the structure of the whole cake provided it is not too thick

Working at constant concentration and initial velocity

$$R_K = r_K \frac{cV}{A} \qquad (5)$$

If these conditions are not fulfilled the integration of equation 4 is not always possible in the absence of a mathematical relation between r_d, c and ΔP

COMPRESSIBLE SLUDGES

For compressible sludges r_d is also a function of p the pressure loss in the liquid in a cake The form of this function cannot be derived from theoretical principles, and it must therefore be deduced from actual measurements, from which can be found the relation between a mean specific resistance, determined by

$$R_K = \int_0^{cV/A} r_d\, d\left(\frac{cV}{A}\right) = r_m \frac{cV}{A} \qquad (6)$$

and the total pressure difference ΔP r_m designates the mean specific resistance of the cake per unit weight per unit of surface

Two types of functions have been deduced exponential functions, $r_m = r'(\Delta P)^a$ (D R SPERRY[20], H C WEBBER and R L HERSHEY[21]), or $r_m = r'[1 + \alpha(\Delta P)^a]$ (B F RUTH[22]), and a linear function, $r_m = r'(1 + \alpha\Delta P)$ (J P M VAN GILSE[12], M B DONALD and R D HUNNEMAN[23]) where r' is a dimensional constant and α, a are dimensionless constants From these approximate integrated expressions nothing definite can be said about the actual influence of p on r_d It can be shown mathematically that an approximate linear function of r_m in ΔP results from an exponential function[8] of r_d in p Moreover the range of pressure differences used might have obscured the actual facts An exponential dependence therefore seems probable Although the second type of formulation seems to be more in accordance with facts because r_d cannot be zero at $p = 0$, it seems a possible approximation with respect to actual results found so far to introduce

$$r_d = r' p^a \qquad (7)$$

(For other examples see Carman) This equation includes also the non-compressible sludges for which $a = 0$ The pressure loss in liquid in a cake, p, ranges from zero (pre-filtration side of the cake) to p_K (post-filtration side of the cake)

Now

$$\frac{1}{A}\frac{dV}{d\theta} = \frac{1}{\mu}\frac{\Delta P}{R_K + R_f} = \frac{1}{\mu}\frac{p_K}{R_K}$$
$$= \frac{1}{\mu}\frac{dp}{dR_K} = \frac{1}{\mu}\frac{dp}{r_d\, d(cV/A)}$$

where p_K is the pressure difference over the cake Introducing equation 7 and integrating between the limits cV/A and 0, p_K and 0, yields

$$\frac{1}{A}\frac{dV}{d\theta} = \frac{1}{\mu}\frac{p_K}{r_1 p_K^a (cV/A)} \qquad (8)$$

where r_1 is a dimensional constant

CLOTH RESISTANCE

Based on the experiments on clean filter cloths[10], A J V UNDERWOOD[24] has given the relation between $(1/A)(dV/d\theta)$ and the filtration pressure as an exponential function in which the exponent changes from 2 to ½ Although the exponent 2 is very unlikely[25], since

$$\frac{1}{A}\frac{dV}{d\theta} = \frac{p_f}{R_f}$$

(p_f being the pressure difference over the filter medium) it may be assumed that

$$R_f = R' p_f^{a''} \qquad (9)$$

R' being a dimensional constant, a'' a dimensionless constant For several reasons it is often not permissible to use the resistance of the clean cloth It may be that in the initial stages of a filtration the filter is clogged or must be clogged to ensure good filtration or, due to experimental conditions, the first layers may have a different specific resistance If the filter is not completely clogged up there is no apparent reason for not introducing the resistance of the encrusted cloth in the equation 3 as long as the amount of clogging is small or known A big disadvantage however is that this resistance can only be found by extrapolation of experimental results, which greatly reduces the accuracy

For the encrusted cloth Carman considers only the cloth-held cake responsible for the modified ' cloth resistance ' R'_f Although this is not a justifiable assumption, his reasoning might serve as a first approximation Treating the cloth-held cake as a normal compressible cake (exponent $0 < a' < 1$) and noting that the pressure on the cake ranges from p_K to ΔP, the following equation is derived with constants R_1 (dimensional) and a' (dimensionless)

$$\frac{1}{A}\frac{dV}{d\theta} = \frac{1}{\mu}\,\frac{(\Delta P)^{(1-a')} - p_K^{(1-a')}}{R_1} \qquad (10)$$

Filtration equation— Combining equations 8 and 10 gives

$$\frac{1}{A}\frac{dV}{d\theta}\left[\mu R_1 (\Delta P)^{a'} + \mu r_1 (\Delta P)^{a}\left(\frac{cV}{A}\right)\right]$$

$$= \Delta P\left[1 + \left(\frac{p_K}{\Delta P}\right)^{(1-a)} - \left(\frac{p_K}{\Delta P}\right)^{(1-a')}\right] \qquad (11)$$

where r_1 is a dimensional constant

For thick cakes $P_K/\Delta P$ approaches unity Then, in addition if a is nearly equal to a',

$$1 + \left(\frac{p_K}{\Delta P}\right)^{(1-a')} - \left(\frac{p_K}{\Delta P}\right)^{(1-a')} = 1$$

equation 11 reduces to

$$\frac{1}{A}\frac{dV}{d\theta} = \frac{1}{\mu}\,\frac{\Delta P}{r_1(\Delta P)^{a}\,(cV/A) + R_1(\Delta P)^{a'}} \qquad (12)$$

Therefore

$$r_m = r_1(\Delta P)^{a} \qquad (13)$$

and

$$R'_f = R_1\,(\Delta P)^{a'} \qquad (14)$$

i e for the filtration of compressible sludges the mean specific cake resistance and the cloth resistance may be considered to vary approximately exponentially with the total pressure difference

Considering the right hand side of equation 10, for $p_K/\Delta P \rightarrow 1$, this reduces to $p_f/\mu R_1 p_K^{a'}$, which means that the cloth resistance changes exponentially with the pressure on the upper layer of the cloth[8]

SCOURING EFFECT

In the filtration of slimy precipitates with filter aids a scouring effect was observed[7], the small particles being carried forward faster than the others E A ALLIOTT[8] suggested the introduction of this effect for heterogeneous incompressible sludges also Mathematically this effect has been formulated by considering r_1 to be dependent on the filtration rate

$$r_1 = r_2\left(\frac{1}{A}\frac{dV}{d\theta}\right)^{s} \qquad (15)$$

in which r_2 is a dimensional constant, s a dimensionless constant It has been shown[4], however, that the resulting filtration equation[4, 19] is easily obtained if the cloth resistance is neglected

$$\frac{dV}{d\theta} = \text{const}\,\frac{(\Delta P)^{r}}{V^{m}} \qquad (16)$$

(m, r are dimensionless constants)

Actually at present there is no conclusive experimental support for the influence of scouring effect on filtration If it does occur it would be in the form of a clogging of the porous medium

THE V/θ RELATION FOR CAKE FILTRATION

Equation 12 may serve as a basis to find an approximate relation between V and θ As $V = 0$ for $\theta = 0$, integration of equation 12 yields for a cake filtration at constant pressure

$$(\Delta P)\theta = \mu r_1\,\frac{(\Delta P)^{a} c}{2}\left(\frac{V}{A}\right)^{2} + \mu R_1\,(\Delta P)^{a'}\left(\frac{V}{A}\right) \qquad (17)$$

and at constant rate

$$(\Delta P)\theta = \mu r_1(\Delta P)^{a} c\left(\frac{V}{A}\right)^{2} + \mu R_1\,(\Delta P)^{a'}\left(\frac{V}{A}\right) \qquad (18)$$

As is clear from equation 12 for every cake filtration at constant pressure

$$\frac{dR}{dV} = b \qquad (19)$$

b being a dimensionless constant

Inspection of equation 19 shows that the V/θ relation must be a true parabola or part of a true parabola if the integration constant of equation 19 representing the cloth resistance is not zero This has been pointed out by several authors[14, 20, 21] The relation can be formulated mathematically[14] by assuming the cloth resistance equal to a cake formed by filtering a volume V_0 in the time θ_0 Thus

$$\frac{1}{A}\frac{dV}{d\theta} = \frac{1}{A}\frac{d(V+V_0)}{d(\theta+\theta_0)} = \frac{1}{\mu}\frac{\Delta P}{[r_1(\Delta P)^s c/A]\,[V+V_0]} \tag{20}$$

therefore

$$(V+V_0)^2 = \frac{2A^2(\Delta P)^{(1-s)}}{\mu r_1 c}(\theta+\theta_0) \tag{21}$$

In making calculations for filtration apparatus, equations 17, 18 and 21 or any other integrated result of equation 12 or analogous equations can be used if the different constants are determined in a small scale experiment by appropriate graphical interpretation of the results

C C DE WITT[32] gives a relationship between V and θ_0 in the same form as the Gompertz equation for death and birth rates of populations *i e*

$$f(V) = \text{const} \quad \exp[-\exp\{-f'(\theta)\}] \tag{22}$$

This approach is not very convincing because its physical background is too broad and therefore too vague

SPECIFIC RESISTANCE AND POROSITY

In order to obtain a more detailed picture of the specific resistance of a cake, the results obtained with the filtration through stationary beds of solid particles[33-35] have been used[36] J KOZENY[35] showed that k may be written

$$k = K'\beta\frac{\varepsilon^3}{(1-\varepsilon)^2}\frac{1}{S^2} \tag{23}$$

where β is the shape factor, ε the porosity (volume of void per unit volume of cake), S is the specific surface of solid per unit of volume of solid, and K' is a dimensional constant

For an incompressible cake therefore

$$\frac{1}{A}\frac{dV}{d\theta} = K'\beta\frac{\varepsilon^3}{(1-\varepsilon)^2}\frac{1}{S^2}\frac{p_K}{\mu L} = \frac{Ap_K}{\mu r_K c V} \tag{24}$$

Since $A(1-\varepsilon)L\delta = cV$, δ being the density of solid

$$r_K = \frac{(1-\varepsilon)^2 S^2}{\delta\varepsilon^3 K'\beta} \tag{25}$$

or introducing the void volume ν of cake per unit weight of substance and noting that according to B F RUTH[37] ν^3 is a linear function of $\nu^3\delta/[\nu+(1/\delta)]^2$ and moreover a certain void volume ν_0 is not available for fluid flow, the constant specific resistance, r_K, may be calculated as follows

$$r_K = \frac{S^2 K''}{(\nu-\nu_0)^2\delta} \tag{26}$$

where K'' is a dimensional constant

Little is known at present about porosity as a function of shape, size and size distribution of the solid substance H J FRASER[38] found that the porosity decreases as the average particle size increases, and that for a constant volume ratio of a two component system with decreasing ratio of small particles to large particles after an initial increase over a small region, a decrease in porosity, reaching a constant value, occurred For compressible sludges a knowledge of the changes of void volume with pressure is needed in order to be able to integrate the resulting equation This relationship is not known and again recourse must be taken to experimental observation of the system being studied

More differential expressions analogous to equation 24 for the flow of fluids (especially of gases) through beds of solid particles have recently been given by W K LEWIS *et alii*[39] M LEVA *et alii*[40] and S ERGUN and A A ORNING[41], these refer both to streamline and non-streamline flow conditions L E BROWNELL and D L KATZ[42], comparing the flow of a fluid through a porous mass with the flow through pipes, introduce a modified Reynolds' number and friction factor, both depending on the shape of the particles and the porosity of the cakes, to predict filtration rate An interesting study based on this conception, of the simultaneous flow of two liquids is given for rotary vacuum filtrations This method of attack is important, especially for filtrations with a high filtration rate (also centrifuges)

CLOTH/CAKE RELATIONS

BLOCKING FILTRATION

In the foregoing discussion some clogging of the porous medium has been accepted which clogged the cloth without impeding the cake above it The only important problem about this system was the knowledge of the actual resistance of the filter cloth Whereas this occurs for all industrial filtrations with cakes of a certain thickness, it has been indicated[43] that there are many industrial filtrations in which the cloth/cake relationship plays the most important part This occurs for instance with dilute suspensions of slimy particles (rayon industry) Knowledge of the cloth/cake relationship is therefore important This statement holds good in general for every filtration because the initial stage of every sludge and water filtration is governed by this relationship Moreover the phenomenon of blocking is a general one, its effects depending on filtration conditions P H HERMANS and H L BREDEE[44] have derived laws for three different cases of blocking

$$
\begin{aligned}
&1\ dR/dV = b'R^2 \text{ (complete blocking)}\\
&2\ dR/dV = b''R^{3/2} \qquad (27)\\
&3\ dR/dV = b'''R
\end{aligned}
$$

To this series the cake filtration may be added

$$4\ dR/dV = b$$

In these representations $b' - b'''$ are dimensionless constants

The author is of the opinion that the change from complete blocking to cake filtration is a gradual one *i e* $dR/dV = b''''R^q$, the value of q ranging from 2 to zero The magnitude of q depends on the system to be filtered, the porous medium, and filtration conditions An extrapolation to $V = 0$ of the R/V relationship found in filtration usually yields values for the cloth resistance which are different from the resistance of the clean filter medium Excluding observations of an uncertain nature, this extrapolated resistance is in general too high This may be caused by a real blocking of the porous medium, or an apparent blocking because conditions of filtration result in a specific resistance of the initial layers of the cake higher than the normal value in the first stages of the filtration that cannot be followed properly Every R/V relationship, provided that it can be measured over the whole range and that conditions are constant, must intersect the V axis at a value equal to the cloth resistance An interesting study about R/V lines for different cases has been given by A BRIEGHEL-MÜLLER[15]

FILTER EFFECT

One of the least understood phenomena in filtration practice and theory is the so-called filter effect (in all probability first described by G F HÜTTIG and M NELLER[44]) on filtering an apparently clear liquid through a porous medium the rate of flow decreases with time This decrease can be very pronounced *e g* when filtering ammonia Several explanations have been given, omitting the obvious effect of algae dissolved air in the liquid freed in vacuum filtration[45], very small solid particles, in suspension, or freed during filtration[7, 33, 43, 46], compression of the filter cloth[47] and electrokinetic forces, that give rise to an electro-osmotic flow region which increases with time, decreasing the actual flow region[37] It is obvious from experiments with solutions containing ions that with small capillaries this last fact plays an important part It cannot, however, be a general cause and probably most of the factors mentioned, or combinations of these, have some influence

A good remedy against the very inconvenient filter effect is the use of prefiltered liquid[46,48] In practice this precaution is not always possible

INFLUENCES ON RATE OF FLOW

Ionic influence—It may be remarked that electrokinetic phenomena can also influence the specific resistance of a cake By reducing the electro-osmotic flow region with ions, the resistance of a cake can be reduced[41] Moreover the size of flocculates can be altered by changing their charge Addition of a peptizing agent can increase the resistance of some slurries considerably

Surface tension influence – The effect of the surface tension of the liquid has not been dealt with in much detail E E JEWETT and R E MONTONNA[8] observe an increase in flow on decrease of the surface tension A very marked similar effect for gelatinous products has been patented[49]

WASHING A CAKE

In principle the rate of washing can easily be determined by using the filtration equations with constant resistance In general, however, the conditions during washing are not the same as those during filtration Cracks can be formed, the cake formation may alter and the path of the liquid can be different (filter presses) In general the use of conditions at the end of a filtration as a basis for estimating the washing time is open to question

Moreover even if this time could be calculated, nothing definite can be said so far about the process of washing a cake free from mother liquor, because this will depend on the distribution of pores in the cake as well as on the diffusion into the streaming liquid Such an effect must again be determined experimentally

CONCLUSIONS

Some aspects of the factors determining the filtration rate have been discussed With regard to industrial filtration, problems of plant-scale operation can be handled approximately provided that proper attention can be given to such factors as temperature (influence on viscosity and probably on specific resistance), exact known working conditions, homogeneity of suspension, sedimentation in the apparatus (uneven cakes), and absence of vibration Greater success would be reached if it were fully recognized that filtration is a complicated process and if every factor governing the process could be clearly separated and included in the observations and conditions

It is obvious that the theory is still very far from complete The lines along which further research must be carried out will not be discussed here, but one item is outstanding the specific resistance must be broken down into variables which can be measured easily without the use of individual filtration experiments for every system

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Heat of Atomization of Carbon

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THE heat of atomization of carbon is the enthalpy change ΔH accompanying the transformation of 1 gm atom of carbon from graphite * to free ground state (^3P) atoms, ΔH_{atom} $C_{graphite}$ the latent heat of sublimation of graphite which, for the sublimation transformation at 0°K, has been designated[1] L Apart from its intrinsic interest, this energy term is directly involved in all absolute bond energy treatments and in all applications of molecular structural ideas to thermochemical data, in organic chemistry

The unequivocal evaluation of this important quantity has not yet been achieved, despite a great weight and variety of experimental evidence, especially by the analysis of spectroscopic data, particularly for CO, and thermodynamic and kinetic data The uncertainty in the evaluation of L is not that of a wide range within which the true value must fall but of the choice, essentially, between four accurately known alternative values, 170 4, 141 2, 136 1 and 125 0 kcal/gm atom, while the value 73 6 kcal/gm atom (k/a) also has its advocates

The experimental methods for investigating the problem may be divided into two classes

1 Indirect methods based on investigation of the energy levels of simple gaseous carbon compounds by spectroscopic, photochemical, electron impact, thermochemical and kinetic methods

2 Direct methods, in which the actual sublimation change

$$C_{graphite} \dashrightarrow C_{atom}\ (^3P)$$

is investigated and the latent heat of sublimation L is evaluated from, for example measurements of vapour pressure or of rate of loss of weight

INDIRECT METHODS

The energy units employed by spectroscopists [electron volts (ev) or frequencies (cm^{-1})] and thermochemists [kilocalories (k)] are related as follows

$$1\ \mathrm{ev} = 23\ 06\ \mathrm{k}$$
$$1\ \mathrm{cm}^{-1} = 2\ 858 \times 10^{-3}\ \mathrm{k}$$

Spectroscopic data yield ΔH values associated with transformations at 0°K, ΔH_0 terms, while thermochemical treatments use ΔH values for transformations at 298°K, ΔH_{298} terms The conversion factors[2] are relatively small and

$$(\Delta H_{298})_{atom}\ C_{graphite} = L + 1\ 2\ \mathrm{k/a}$$

The compounds which have been most used in the indirect approach to L are CO, CH_4, C_2N_2 and C_2H_2 The procedure, the same in principle for each compound, is illustrated by the CO investigation which is formally the simplest and has been the most intensively pursued

The energy levels of the CO system involved in the investigation are shown in *Figure 1*

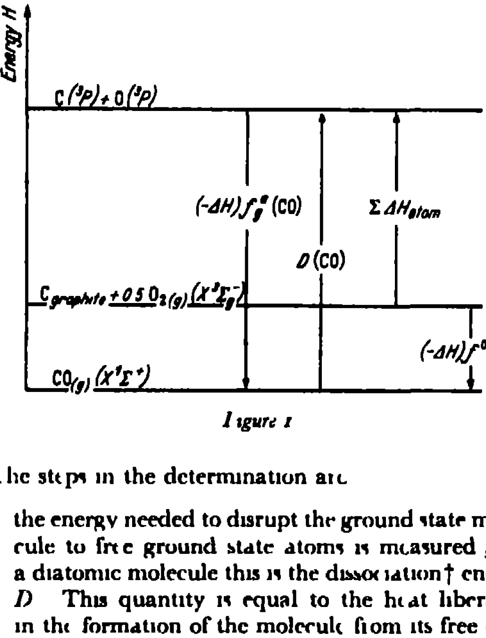
Energy H
C (^3P) + O (^3P)
$(-\Delta H)f^{\circ}_{g}$ (CO)
$\Sigma\Delta H_{atom}$
D (CO)
$C_{graphite}$ + 0 5 $O_{2(g)}$ $(X^3\Sigma_g^-)$
$(-\Delta H)f^{\circ}$ (CO)
$CO_{(g)}$ $(X^1\Sigma^+)$

Figure 1

The steps in the determination are

a the energy needed to disrupt the ground state molecule to free ground state atoms is measured, for a diatomic molecule this is the dissociation† energy D This quantity is equal to the heat liberated in the formation of the molecule from its free constituent atoms $(-\Delta H)f^{\circ}_{g}$ *i e* 'the atomic heat of formation'

b the energy liberated in the formation of the molecule from its constituent elements in their standard states $(-\Delta H)f^{\circ}$ *i e* 'the heat of formation, standard state', is measured

The difference between $(-\Delta H)f^{\circ}_{g}$ and $(-\Delta H)f^{\circ}$ gives the sum of the heats of atomization of the constituent elements $\Sigma\Delta H_{atom}$, and ΔH_{atom}(C) follows from a knowledge of the ΔH_{atom} terms for the other constituent elements For CO

$$\Sigma\Delta H_{atom}(\mathrm{CO}) = \Delta H_{atom}(\mathrm{C}) + \Delta H_{atom}(\mathrm{O})$$

---

* Graphite is the reference state now universally accepted for solid carbon[1]

† Unless other specifications are quoted D refers to the dissociation of the ground state molecule to ground state atoms

where

$$\Delta H_{atom}(\mathrm{O}) = 0.5\,D(\mathrm{O_2})$$

The application of this method to each of the molecules follows

The CO molecule

$$L = D_0(\mathrm{CO}) - 0.5\,D_0(\mathrm{O_2}) - (-\Delta H_0)f^0(\mathrm{CO})$$

$$(-\Delta H_0)f^0(\mathrm{CO}) = 27.18 \text{ kcal/mol}[4]$$

$D_0(\mathrm{O_2}) = 5.084$ ev (from spectroscopic work reviewed by G HERZBERG[5] and by A G GAYDON[6] Inserting these values in the above expression we have

$$L = D_0(\mathrm{CO}) - 85.8 \text{ k/a}$$

$D_0(\mathrm{CO})$ *1 Spectroscopic evidence* - The spectrum of CO is complex and susceptible to variations of interpretation, *Figure 2* Critical reviews by G HERZBERG[5], A G GAYDON[6] and H D HAGSTRUM[7] have appeared

The value taken for $D_0(\mathrm{CO})$ is based primarily on the observation of the vibrational levels of the ground state $X^1\Sigma^+$ and the $a'^3\Sigma^+$ state Analysis may be simplified by taking the problem in two parts

i Energy intervals - The energy interval between the lowest vibrational level ($v = 0$) for $\mathrm{CO}(X^1\Sigma^+)$ and the convergence limit of $\mathrm{CO}(a'^3\Sigma^+)$ is 11.11 ev This is based on tracing[8] the vibrational levels of $\mathrm{CO}(a'^3\Sigma^+)$ up to $v = 41$ leaving a short extrapolation to the convergence limit, and on the evaluation at 6.90 ev of the energy interval between the $v = 0$ levels of the $X^1\Sigma^+$ and $a'^3\Sigma^+$ states from the Hopfield-Birge bands

There is still doubt as to the location of the convergence limit for $\mathrm{CO}(X^1\Sigma^+)$ The vibrational levels have only been traced up to $v = 22$ which is still far below the convergence limit so that there is uncertainty in the long extrapolation Reasonable arguments, based on predissociation phenomena and on Birge-Sponer extrapolation, have been advanced in favour of two different locations at 9.14 ev using an orthodox curvilinear extrapolation[5, 9], and at 11.11 ev using a linear extrapolation[10]

ii Dissociation products— There is no reasonable doubt that the products from the dissociation of $\mathrm{CO}(X^1\Sigma^+)$ are ground state atoms[5, 6], $\mathrm{C}(^3P)$ and $\mathrm{O}(^3P)$ There is, however, no certainty as to the excitation of the C and O atoms produced by the dissociation of $\mathrm{CO}(a'^3\Sigma^+)$ Of six different sets of possible products[6] $\mathrm{C}(^3P) + \mathrm{O}(^3P)$ and $\mathrm{C}(^3P) + \mathrm{O}(^1D)$ are the most important

There are therefore two main alternative interpretations of the data, shown in *Table I*

Table I

	CO state	Dissociation: Products C	O	Energy D_0 ev	L k/a implied
I	$X^1\Sigma^+$	^3P	^3P	9.14	125.0
	$a'^3\Sigma^+$	^3P	^1D	4.91	
II	$X^1\Sigma^+$	^3P	^3P	11.11	170.4
	$a'^3\Sigma^+$	^3P	^3P	4.91	

G HERZBERG[3, 5, 6] has favoured the first view (*Figure 2c*) while A G GAYDON and W G PENNEY[10] have recently brought forward evidence, based largely on the non-crossing rule[11, 12], in favour of the second view (*Figure 2a*) Their evidence has been questioned, though not disproved[9, 13]

Very recently[11], D for $\mathrm{CO}(F^1\Pi)$ has been estimated as 0.5 ± 0.3 ev This value is based on the anharmonicity of vibrational motion in this electronic level and cannot be greatly in error The dissociation process is probably

$$\mathrm{CO}(F^1\Pi) \longrightarrow \mathrm{C}(^1D) + \mathrm{O}(^1D)$$

giving for

$$\mathrm{CO}(X^1\Sigma^+) \longrightarrow \mathrm{C}(^3P) + \mathrm{O}(^3P)$$
$$D_0 = 9.6 \pm 0.3 \text{ ev}$$

This third value for $D_0(\mathrm{CO})$ is in close agreement with the value[14] advocated from electron impact experiments and is reconcilable with the predissociation at 11.11 ev if $\mathrm{CO}(a'^3\Sigma^+)$ dissociates to $\mathrm{C}(^1D) + \mathrm{O}(^3P)$, *Figure 2b*, see below

A fourth value for $D_0(\mathrm{CO})$, 6.92 ev has been advanced[16-18] based on the claimed observation of a predissociation in the $A^1\Pi$ state and also assuming that $\mathrm{CO}(X^1\Sigma^+)$ dissociates at 11.11 ev to $\mathrm{C}(^5S)$ and $\mathrm{O}(^3P)$ There is doubt about the existence of this predissociation[9], moreover, such a low value for $D_0(\mathrm{CO})$ would imply serious violations of the non-crossing rule and a value of $L = 73.9$ k/a so low as to be virtually irreconcilable with the thermochemistry of carbon compounds

$D_0(\mathrm{CO})$ *2 Photodissociation*— Experiments on the photodissociation of CO have been claimed[19] to indicate that $D_0(\mathrm{CO})$ must lie in the range 8.44 to 9.57 ev but the conclusions as to $D_0(\mathrm{CO})$ from this work are not rigid[10]

$D_0(\mathrm{CO})$ *3 Electron impact dissociation*—— H D HAGSTRUM and J T TATE[14] have interpreted the results of electron impact measurements on CO as indicating that $D_0(\mathrm{CO}) = 9.6 \pm 0.2$ ev The interpretation of the complex data has been questioned[9, 10] Hagstrum has however recently[7] given a treatment of the CO spectrum in which he attributes the predissociation at 11.11 ev to the existence of a maximum in the potential curve for the $a'^3\Sigma^+$ state, this state

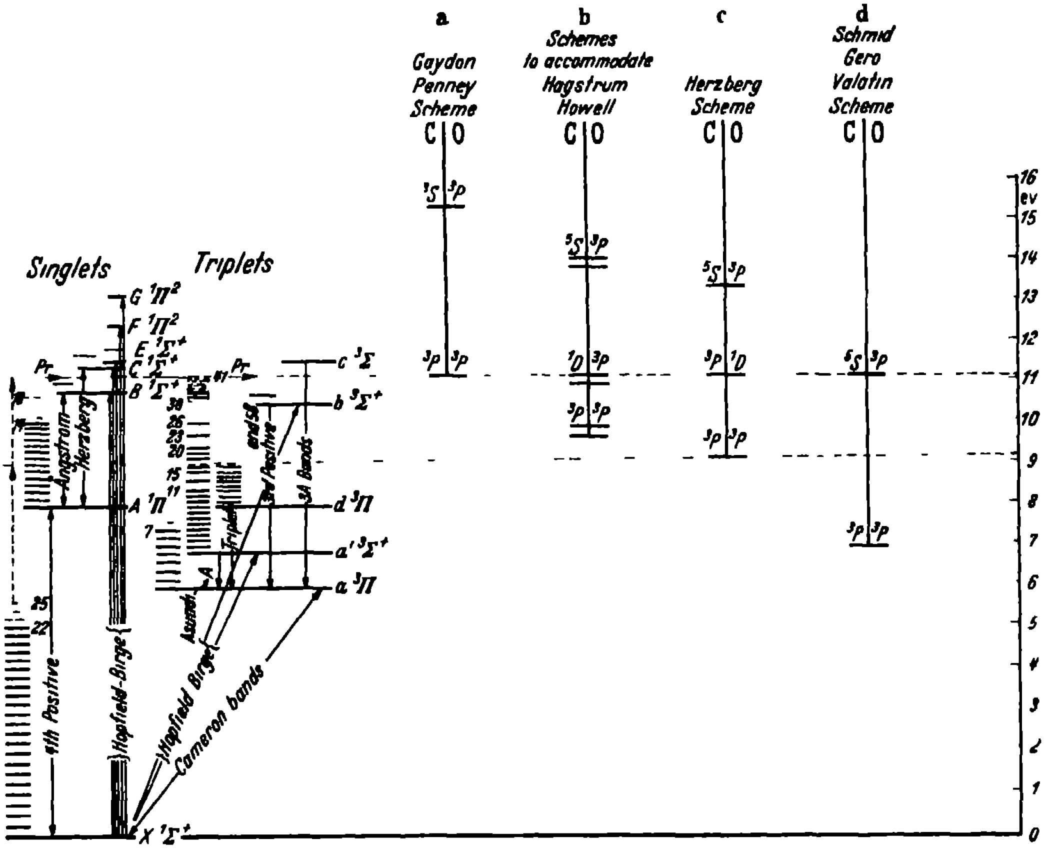

Figure 2 *Energy level diagram of* CO *The main predissociations are indicated by Pr*

dissociating at 10 87 ev to C(^1D) + O(^3P) and thus reconciles all data with D_0(CO) = 9 61 ev Gaydon has pointed out[8] that on the more orthodox interpretation of the CO spectrum, accepting the dissociation of CO($a'^3\Sigma^+$) at 11 11 ev, then, assuming that the products are C(^1D) + O(^3P), D_0(CO) = 9 85 ev it is possible to regard the electron impact work [and the results on CO($F^1\Pi$)] as indicating D_0(CO) = 9 61 or 9 85 ev, the former seeming preferable to the latter[20] (*Figure* 2b) Such values for D_0(CO) imply violations of the non-crossing rule[8]

The data on D_0(CO) therefore yield five possible results of which four (11 11, 9 85, 9 61 and 9 14 ev) are much more probable than the fifth (6 92 ev) A final choice between the four more probable values does not seem possible at this stage though the weight of evidence seems to favour the 11 11 and 9 61 ev values These D_0(CO) values permit, respectively, the five alternative values for L, 170 4, 141 2, 136 1, 125 0 and 73 6 k/a and exclude all other values

The CH$_4$ *molecule*

$$^{4}L = \Sigma D_0(\mathrm{CH_4}) - (-\Delta H_0)f^{\circ}(\mathrm{CH_4}) - D_0(\mathrm{H_2})$$

where

$$\Sigma D_0(\mathrm{CH_4}) = D_0(\mathrm{CH_3{-}H}) + D_0(\mathrm{CH_2{-}H}) + D_0(\mathrm{CH{-}H}) + D_0(\mathrm{C{-}H})$$

$$(-\Delta H_0)f^{\circ}(\mathrm{CH_4}) = 15\ 99\ \mathrm{k/m}^{4}$$

$$D_0(\mathrm{H_2}) = 4\ 4776\ \mathrm{ev}$$

(from spectroscopic work discussed in the two reviews) thus

$$L = \Sigma D_0(\mathrm{CH_4}) - 222\ 4\ \mathrm{k/a}$$

ΣD_0(CH$_4$) of the four terms involved in the summation only two, D_0(CH$_3$–H) and D_0(C–H), have been measured directly

D_0(CH$_3$—H) G B KISTIAKOWSKY and his collaborators have studied the kinetics of the photochemical bromination of methane[21, 22] and by combining the results with thermochemical and pyrolytic data have obtained the value of 101 + 1 k/m for D_0(CH$_3$—H) Electron impact experiments[23] also indicate D_0(CH$_3$—H) = 101 k/m

D_0(C—H) Spectroscopic predissociation evidence[24] on CH($^2\Pi$) gives D_0(C—H) = 3 47 ev

This derivation seems acceptable to spectroscopists[5, 6] The data on the $^2\Pi$ state has been found[7, 8] to be compatible with work on the $^2\Sigma$ state

D_0(CH$_2$-H) and D_0(CH—H) there is no direct experimental evidence leading to an evaluation of these energy terms Two sets of electron impact data can be combined* to give for

$$CH_4 \longrightarrow CH_2 + H_2$$
$$\Delta H = 3\ 8 \pm 0\ 7 \text{ ev}$$

which combined with D_0(CH$_3$—H) and D_0(H$_2$) gives a value for D_0(CH$_2$—H) = 90 ± 16 k/m The rather wide limits of experimental error lessen the value of this estimate

The complex literature on the chemical kinetics of reactions involving the CH$_2$ and CH$_3$ radicals has been reviewed by F W R **Steacie**[27] There is frequently great difficulty in deciding the reaction mechanisms corresponding to observed kinetic data and in measuring the activation energies of both forward and backward reactions of a given equilibrium, so that the results from this field are rather unhelpful in the assessment of ΔH terms corresponding to definite reactions involving CH$_2$ and CH$_3$, from which D_0(CH$_2$—H) could be evaluated, although such evaluations have been attempted[28]

In the absence of experimental data, the problem of calculating D_0(CH$_2$-H) and D_0(CH—H) has been attacked There are two main effects influencing the variation of the D_0(C—H) terms as successive H atoms are removed from CH$_4$ First, the H ⟵⟶ H repulsion forces fall off this tends to increase successive D_0(C—H) terms, and secondly the nature of the C orbital involved in the C—H bond changes from the sp^3 orbital in CH$_4$ to the p orbital in CH, which tends to decrease successive D_0(C—H) terms

A completely satisfactory theoretical consideration of these two effects in the stepwise dissociation of CH$_4$ has yet to be given, though J H **van Vleck**[29] has laid the foundations of such a treatment This approach has been developed by W G **Penney**[30] and H H **Voge**[26, 31] using experimental data to help in the evaluation of certain of the integrals involved Voge, using the experimental values for D_0(CH$_3$—H) and D_0(C—H), has calculated

$$D_0(CH_2—H) = 88\ 1 \text{ k/m}$$
$$D_0(CH—H) = 79\ 6 \text{ k/m}$$

G **Glockler**[32] has estimated D_0(CH$_2$—H) and D_0(CH—H) as 93 k/m and 86 k/m respectively but his method involves such serious assumptions as to render the estimates of little value in themselves A D **Walsh**[33] has given a qualitative treatment to the problem of the bond energies of CH$_2$ and CH$_3$, considering the changes in the relative electronegativities of the C and H atoms of the C—H bond, with changes in C orbital hybridization He suggests

$$D_0(CH_2—H) \sim D_0(CH—H) \sim 85 \text{ k/m}$$

The data are insufficient to permit rigid evaluation of ΣD_0(CH$_4$) but some information as to the magnitude of L can be obtained Since ΣD_0(CH$_4$) = L + 222 k/m then, if the values of 101 and 80 k/m respectively for D_0(CH$_3$—H) and D_0(C—H) are accepted

$$D_0(CH_2—H) + D_0(CH—H) = L + 41 \text{ k/m}$$

By inserting in this expression the various values of L permitted by the CO data, permissible values for the sum of the two D_0 terms can be set down, *Table II*

Table II

L k/a	D_0(CH$_2$—H) + D_0(CH—H) k/m
170	211
141	182
136	177
125	166
74	115

Now, all the evidence seems to show that both D_0(CH$_2$—H) and D_0(CH—H) must ⩾ D_0(C—H) *i e*

$$D_0(CH_2—H) + D_0(CH—H) \geqslant 160 \text{ k/m}$$

the most probable actual value coming from Voge's[26] data and being 170 k/m so that, by this approach, the CH$_4$ data do virtually eliminate the lowest value of L (74 k/m) Any of the intermediate values for L could be accommodated, the values 125 and 136 k/a somewhat more readily than that of 141 k/a The highest value (170 k/a) is not favoured by these considerations but is not excluded

L H **Long** and R G W **Norrish**[34-36] have worked on the problem of evaluating L from data on CH$_4$ using a somewhat different approach They regard the dissociation energy of a given bond *e g* D_0(CH$_3$—H) as the difference between the 'bond energy' E of the bond in the parent system (here, the CH$_4$ molecule) and the 'reorganization energy' of the resulting system (here, the CH$_3$ radical) They identify the state of the C atom in CH$_4$ as atomic C(^5S), assume that $E(C—H)_{CH_4} \sim E(C—H)_{CH_3}$, and evaluate $L \sim 182 - X$ k/a, where X is the ΔH for the change C(^3P) ⟶ C(^5S) a result then indicating L = 125 k/a But since the experimental evaluation of X as 96 4 k/a[36, 37] and the challenging of the two underlying assumptions[39, 40] the Long-Norrish treatment of the CH$_4$ data cannot be accepted as final evidence in favour of the 125 k/a value for L The CH$_4$ data do not therefore offer a clear decision on the value of L though the weight of evidence is probably in favour of the value L = 136 k/a

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* Private communication from D P **Stevenson** to H H **Voge** and discussed by the latter[26]

The C_2N_2 *molecule*

$$L = 0\ 5[\Sigma D_0(C_2N_2) - (-\Delta H_0)f^{\circ}(C_2N_2) - D_0(N_2)]$$

where

$$\Sigma D_0(C_2N_2) = D_0(\mathrm{NC{-}CN}) + 2D_0(\mathrm{CN})$$

None of the terms necessary to evaluate L by the above expression is known with complete accuracy

$(-\Delta H_0)f^{\circ}(C_2N_2)$ the most probable value[41] is 71 4 k/m

$D_0(N_2)$ is the subject of a controversy outside the scope of this review Spectroscopic evidence permits the two alternative values of 7 38 ev[8] and 9 76 ev[9] The position is analogous to that of the 9 14 and 11 11 ev values for $D_0(\mathrm{CO})$

$D_0(\mathrm{NC{-}CN})$ Several experimental values have been reported for this term Using the optical estimation of the change of concentration of CN in C_2N_2 with temperature, G B KISTIAKOWSKY and H GERSHINOWITZ[42] derived the very low value 77 k/m J U WHITE[43] has given good reasons for rejecting this value and advocates the value 146 + 4 k/m with 138 k/m as an independently estimated lower limit Kinetic investigation of the thermal reaction of H_2 and C_2N_2[44] and the photo-polymerization of C_2N_2[45], indicate values of 127–130 k/m L H LONG[46] derives a value of 115 k/m for $D_0(\mathrm{NC{-}CN})$ from a value for $D_0(\mathrm{CH_3{-}CN})$ derived from the long wavelength limits of the second region of continuous absorption in the acetonitrile spectrum He supports this evaluation with similar treatments for ICN and HCN A value (120 ± 8 k/m) has been derived[47] based on Born-Haber cycles for NaCN and KCN, a treatment involving assumptions as to the crystal lattice energies and the electron affinity of CN

$D_0(\mathrm{CN})$ R SCHMID L GERO and J ZEMPLEN[48] have succeeded in fixing by a short extrapolation the convergence limit of $\mathrm{CN}(A\,\Pi)$ at 7 50 ± 0 12 ev above $v = 0$ for the $X^2\Sigma^+$ ground state (The vibrational levels in the ground state also extrapolate to this convergence limit) They suggested that the $A^2\Pi$ and $X^2\Sigma^+$ states of CN dissociate to $\mathrm{C}(^3P) + \mathrm{N}(^2P)$, so that for the dissociation

$$\mathrm{CN}(X^2\Sigma^+) \longrightarrow \mathrm{C}(^3P) + \mathrm{N}(^4S)$$
$$D_0(\mathrm{CN}) = 3\ 93 \text{ ev}$$

L H LONG[46] has suggested that $\mathrm{CN}(A\,\Pi)$ might dissociate to $\mathrm{C}(^3P) + \mathrm{N}(^2D)$, giving $D_0(\mathrm{CN}) = 5\ 09$ ev A G GAYDON has however recently shown[9, 10] that it is much more probable that $\mathrm{CN}(X^2\Sigma^+)$ and $(A^2\Pi)$ both dissociate directly to ground state atoms so that $D_0(\mathrm{CN}) = 7\ 50$ ev The bearing of these cyanogen data on the problem of L has been the subject of several discussions

G HERZBERG[9] assessed the merits of the various experimental values for $D_0(\mathrm{NC{-}CN})$ by considering the relative magnitudes of $D_0(\mathrm{NC{-}CN})$ and $D_0(\mathrm{CN})$ implied by the experimental $D_0(\mathrm{NC{-}CN})$ values on the alternative assumptions of $L = 125$ or 170 k/a, using the lower value of $D_0(N_2) = 7\ 38$ ev, the value of $D_0(N_2)$ universally accepted at that time (1942) He favoured $D_0(\mathrm{NC{-}CN}) = 77$ k/m and $L = 125$ k/a, implying $D_0(\mathrm{CN}) = 5\ 98$ ev, but his argument is even better met by the hypothesis $L = 170$ k/a and $D_0(N_2) = 9\ 76$ ev (only available since 1944) than by the hypothesis[3] $L = 125$ k/a and $D_0(N_2) = 7\ 38$ ev

A second treatment has been given by the present author[8] accepting $D_0(\mathrm{NC{-}CN}) = 142$ k/m, $D_0(\mathrm{CN}) = 7\ 50$ ev and following two lines *a* comparing the atomic heat of formation of C_2N_2, $(-\Delta H)f^{\circ}_g(C_2N_2)$, given by the expression

$$D_0(\mathrm{NC{-}CN}) + 2D_0(\mathrm{CN}) = (-\Delta H)f^{\circ}_g(C_2N_2) = 400 \text{ k/m}$$

with the four values given by the expression

$$-(\Delta H)f^{\circ}_g(C_2N_2) = 2L + D_0(N_2) + (-\Delta H)f^{\circ}(C_2N_2)$$

using $L = 125$ or 170 k/a and $D_0(N_2) = 7\ 38$ ev or 9 76 ev Of these four values only that from $L = 170$ k/a and $D_0(N_2) = 9\ 76$ ev (497 k/m) falls near the 490 k/m 'experimental' value

b By comparing the accepted $D_0(\mathrm{NC{-}CN})$ and $D_0(\mathrm{CN})$ values with the four sets of values calculated, rather roughly, for these D terms, from the bond energy terms for C—C and C—N on the four different possibilities for L and $D_0(N_2)$ Here, too, there is good agreement only with the values calculated with $L = 170$ k/a and $D_0(N_2) = 9\ 76$ ev The possible loopholes in this analysis are the acceptance of the White value for $D_0(\mathrm{NC{-}CN})$ and the Gaydon identification of the products of the dissociation of the CN radical at 7 50 ev

Long[46] using $D_0(\mathrm{NC{-}CN}) = 115$ k/m, and combining with data on CO finds

$$D_0(\mathrm{CO}) = D_0(\mathrm{CN}) - 0\ 5D_0(N_2) + 170 \text{ k/m}$$

Using $D_0(\mathrm{CN}) = 5\ 09$ ev, this equation is compatible with $D_0(\mathrm{CO}) = 9\ 14$ ev (*i e* $L = 125$ k/a) and $D_0(N_2) = 7\ 38$ ev The value used here for $D_0(\mathrm{NC{-}CN})$ rests ultimately on the long wavelength limits value for $D_0(\mathrm{CH_3{-}CN})$, and this method of estimating D values is open to objection, while the value used for $D_0(\mathrm{CN})$ depends on the somewhat arbitrary choice of $\mathrm{C}(^3P) + \mathrm{N}(^2D)$ as the dissociation products for $\mathrm{CN}(A^2\Pi)$

G GLOCKLER[47] assuming $D_0(\mathrm{NC{-}CN}) = 127$ k/m calculates $D_0(\mathrm{CN})$ for $L = 125$ and 136 k/a and $D_0(N_2) = 7\ 38$ and 9 76 ev He concludes from the $D_0(\mathrm{CN})$ values that his evidence is in favour of $D_0(N_2) = 9\ 76$ ev and does not discriminate between

L — 125 and 136 k/a for which the calculated D_0(CN) values 6 02 or 6 49 ev are acceptable to him The method used in this treatment to fix D_0(NC—CN) at 127 k/m is not rigid, while the calculated values for D_0(CN) to which the treatment leads are not readily reconciled with the convergence limit at 7 50 ev

The C_2H_2 *molecule*

$$L = 0\ 5[\Sigma D_0(C_2H_2) - (-\Delta H_0)f^0(C_2H_2) - D_0(H_2)]$$

where

$$\Sigma D_0(C_2H_2) = D_0(HC{\equiv}CH) + 2D_0(C{-}H)$$

There are experimental values of varying accuracy for all the quantities used to give L by this expression, thus

$$(-\Delta H_0)f^0(C_2H_2) = 54\ 33\ \text{k/m}^4$$

Combining this with the values $D_0(H_2)$ = 103 22 k/m and D_0(C—H) = 80 k/m gives

$$L = 0\ 5D_0(HC{\equiv}CH) + 55\ 5\ \text{k/a}$$

D_0(HC≡CH) both the heat of the reaction HC≡CH ——→ 2 C—H and the electronic state of the CH radicals produced are uncertain Predissociation phenomena in the far ultraviolet spectrum of acetylene indicate[39] the value of about 187 k/m for the dissociation to two CH radicals, while the value 190 to 230 k/m has been given[40] for the activation energy for this dissociation There are difficulties in assessing D terms for polyatomic molecules from spectral data, and though it has been generally assumed that the observed dissociation is to CH($^2\Pi$) the products[34] may be CH($^4\Sigma$)

The value 187 k/m for D_0(HC≡CH) can be used, at best, to give a very rough upper limit of 150 k/a for L Long and Norrish[36] have reviewed similar difficulties in the way of the rigid interpretation of work on the decomposition of acetylene in the electric discharge[41-43]

The HgR_2 *molecules*

Apart from the attacks based on dissociation energies, thermal data for simple organic molecules have been of use in another way to gain information on L

N V SIDGWICK and the present author[44] have calculated alternative values for the atomic heat of formation of each of the compounds mercury dimethyl, mercury diethyl and mercury diphenyl, using M BERTHELOT's data[45] for the heats of combustion, 432, 735 and 1,565 k/m respectively, and taking L = 125 or 170 k/a Analysing the atomic heats with the help of the known mean bond energy terms for the bonds other than Hg—C, they evaluated the mean bond energy term for the Hg—C bond E(Hg—C) and found it to be 4 ± 2 k/m if L = 125 k/a or 16 ± 2 k/m if L = 170 k/a They point out that, though there is no direct correlation between a given mean bond energy term and the dissociation energies for bonds of that type in polyatomic molecules, nevertheless 4 k/m is an unprecedentedly low value for a mean bond energy term, while 16 k/m, though still very low, is not impossible so that these considerations favour the L value of 170 k/a although in the absence of definite information as to the energy conditions in the free methyl radical, the argument cannot be final[44] Actually, it seems likely that Berthelot's value for the heat of combustion of mercury dimethyl, at least, is rather high, 412 k/m being a more probable value[46] This would change the two alternative values for E(Hg—C) derived from $Hg(CH_3)_2$ data to 11 k/m and 23 k/m without changing the argument

H A SKINNER* has pointed out that the ΔH for the reaction

$$Hg(CH_3)_2 \longrightarrow Hg + 2CH_3$$

can be evaluated at 52 k/m from the heat of combustion of $Hg(CH_3)_2$ 412 k/m, and $D_0(CH_3{-}H)$, 101 k/m, without any assumption as to L He and K HARTLEY[47] have independent thermochemical evidence, from an investigation of the reactions of $Hg(CH_3)_2$ with I_2 and with HgI_2, indicating that the ΔH terms for the decomposition of $Hg(CH_3)_2$ to Hg + 2 CH_3 are of the order 50 to 55 k/m

This approach emphasizes the qualitative aspect of the argument as to L given by Sidgwick and the present author and indicates clearly how it is that a rigid solution cannot be obtained from these molecules any more than from CH_4, without information as to $D_0(CH_2{-}H)$, D_0(CH—H) and D_0(C—H)

Other spectroscopic methods— Theoretical treatment has been given[48] to the short wave fluorescence limits of benzene and to the absorption spectra of butadiene and hexatriene, indicating L = 170 ± 10 k/m The method has, however, been strongly criticized[49]

DIRECT METHODS

These methods are of great technical difficulty because of the very high temperatures needed to achieve measurable sublimation of graphite The results are difficult to interpret because the gaseous carbon produced contains a variable proportion of diatomic C_2 molecules and it has not been rigidly proved that in the monatomic vapour the C atoms are produced in the ^3P ground state Several reviews of the problems involved have been given[50-52] The actual investigations have taken the following lines

1 Equilibrium temperature/pressure measurements on graphite[53, 54] from which values for L in the range 120 to 180 k/a have been derived

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* Private communication

2 Measurements of the rate of evaporation of graphite[64, 66] to dynamic methods, yielding L values in the range 170 to 210 k/a

3 Calculations of vapour pressure/temperature curves for monatomic C vapour[61] on various assumptions as to L, followed by comparison of the derived pressure at 4,000°K with the value of 100 atm observed in J BASSET's work[67, 68] on the triple point of graphite Evidence in favour of $L = 125$ k/a has been adduced from this work

The dynamic methods are open to the objection[4, 56, 61] that owing to the valency state of carbon in graphite being related to the ^5S atomic state there may be a 'potential hill' to be surmounted in the evaporation process to $C(^3P)$

This confused position has recently been much clarified by the work of L BREWER, P W GILLES and F A JENKINS[69] They have obtained total vapour pressure/temperature data for graphite by an equilibrium method, that of the effusion of gas through a small knife-edged orifice, and have also determined the partial pressure of C_2 gas in equilibrium with graphite by spectroscopic methods The results lead to the conclusions that *1* $C_2(g)$ in the ground state $(^3\Pi)$ dissociates to $C\ (^3P)$ and *2* 'carbon evaporates from the solid as monatomic gas in the ground electronic state', and to the following values for the critical ΔH_0 terms for the reactions

$$2C_{graphite} \longrightarrow C_2(^3\Pi)\ (g)\ \Delta H_0 \quad 233\ 1$$

$$C_2(g)\ (^3\Pi) \longrightarrow 2\,C\ (^3P)\ \Delta H_0 = 107\ 7\ \text{k/m}$$

$$C_{graphite} \longrightarrow C(^3P)\ \Delta H_0$$

$$\text{i e}\ L = 170\ 39 \pm 0\ 2\ \text{k/a}$$

These findings have been criticized[70] mainly on the basis of Basset's determination of the triple point of carbon which, if $L = 170$ k/a, must involve a large underestimation error in temperature measurement

L BREWER has met this criticism[71] by pointing out that (as mentioned in an earlier paper[69]) under the conditions used by Basset smoke would interfere seriously with the optical pyrometry and would lead to temperature recordings far below reality

SUMMARY

From the rather conflicting mass of evidence considered above it appears that *no single evaluation* of L has yet been made which is acceptable to all workers in the field The final choice is still to be made from among the four possible values, 170 4, 141 2, 136 1 and 125 0 k/a It is, however, perhaps permissible to give some assessment of the apparent relative probabilities of these three values These seem to the reviewer to be as follows

prob (170 4) > prob (136 1) > prob (141 2) > prob (125 0)

It is seen that $L = 170\ 4$ k/a is readily accommodated by the spectral data on the lower electronic states of CO and on C_2N_2 and is given by the latest direct estimation This value is supported by the data from organo-mercury compounds It is not supported but is not excluded by the incomplete CH_4 data at present available The value is opposed by the electron impact data, and to a lesser extent by the spectral work on the $F^1\Pi$ state of CO

$L = 141\ 2$ k/a and $L = 136\ 1$ k/a neither value seems to be very readily assimilated into the CO spectral data derived from the $X^1\Sigma^+$ and $a'^3\Sigma^+$ states though both are supported by work on the $F^1\Pi$ state They are also supported by the electron impact work (the 136 1 k/a value more strongly) and can be readily accommodated but are not strongly favoured by the CH_4 data The support derived for them from the C_2N_2 data seems rather weak No evidence for these values has yet come from direct determinations

$L = 125\ 0$ k/a is the more serious rival to the 170 4 value from the investigation of the lower electronic bonds of the CO spectrum The weight of evidence seems against it even there, however The $CO(F^1\Pi)$ investigation opposes this value, so do the electron impact work and the data from organo-mercury compounds The value can be accommodated by the CH_4 data but does not derive conclusive support from them The support derived for it from C_2N_2 data does not seem very strong, while that derived from direct estimations has lately been convincingly attacked

Among the points needing further investigation are *1* the higher vibrational levels of CO $(X^1\Sigma^+)$, *2* all stages, after the first, in the stepwise dissociation of CH_4, *3* the dissociation of C_2N_2 to CN radicals

Since the above review was prepared (May 1949) a new attack has been made[72, 73] on evaluation of the energy of the C atom in its valence state (the hybridized sp^3 derived from the atomic ^5S) From CH and C_2 data a case is made for setting the valence state energy for $C = 1\ 73$ ev, this combined with CO and C_2N_2 data yields $D_0(CO) = 9\ 77$ ev and $L = 140$ k/a *Although, as recognized by the original authors*[73], certain new postulates are involved in the treatment which cannot be finally accepted until further checking is possible, nevertheless this work adds considerable weight to the Hagstrum-Gaydon view that the predissociation at 11 11 ev in $CO(a'^3\Sigma^+)$ is due to dissociation to $C(^1D)$ and $O(^3P)$ giving $D_0(CO) = 9\ 61$ or $9\ 85$ ev and $L = 136$ or 141 k/a

NOTE ADDED IN PROOF

Even more recently, C A McDowell and J W Warren[74] have subjected methane to an intensive electron impact investigation and have measured, with greater accuracy than heretofore, the appearance potentials of the following ions, CH_4^+, CH_3^+, CH_2^+, CH^+ and C^+. By making reasonable assumptions concerning ionization potentials they assign upper limits to D_0 (CH_3-H) and D_0 ($CH-H$) and conclude that L cannot possibly be > 140 k/a

All this more recent work seems to favour the lower values for L, as opposed to the 170·4 k/a value, and the 136·1 k/a value appears to hold the field at the moment (April 1950) The acceptance of this value for L implies, however, the abandonment of the non-crossing rule and demands a satisfactory alternative interpretation of the work of Brewer *et alii*[69]

The reviewer wishes to acknowledge very helpful discussions with Professors N V Sidgwick, F R S, and M Polanyi, F R S, Drs H A Skinner and L H Long

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Sound Writing and Reading

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MAN has always been interested in transmitting his experiences and expressing his wants to others He has not only devised for this purpose a spoken language but also sets of symbols which preserved and conveyed these messages The early stages of picture writing led eventually to accepted symbols of written and printed communication in which these symbols no longer pictured either the recorded event or any associated factors

Considerable thought has been given in recent years towards the development of methods involving a reversion to some system of recording speech in which the visible symbols are not arbitrarily selected but produced by the sound waves themselves The sound track of motion picture film is of this type but it can be reconverted to speech sounds only by the use of proper scanning devices operating through electrical circuits It is not possible to 'read' such sound tracks in a visual examination It has been the primary goal of recent research to produce permanent or semi-permanent visible speech traces in such form that they may be read by the viewer at the rate of speech This is sound writing and reading

The self-production of sound traces forms a relatively old field of study but the reading of the patterns is a recent and especially significant development The phonautograph, perfected nearly a century ago by L SCOTT[1], had a stylus attached to a membrane which recorded the vibrations produced by the sound impinging on it as a visible trace on moving smoked paper Fifty years later D C MILLER[2] substituted a tiny mirror and a beam of light for the stylus to produce the phonodeik This reduced the inertia of the system and the wave recorded on moving photographic film came somewhat closer to the original sound wave form Even with the increased sensitivity only the major fluctuations appeared and emphasis was given to the low frequency components of long duration

We are here concerned with the possibility of reading the sound traces of spoken words back into speech This study is supported by several stimuli First, the wave pattern of speech is its visible record and furnishes a possible new avenue for communication with the deaf The visible sound wave pattern, which includes the contribution of all the vibrating elements involved in speech and is similar to the energy producing hearing, should be an even more appropriate means than lip reading of transferring intelligence The second stimulus for study lies in the fact that the form of the pattern shows visibly the variations in speech between individuals, and may serve as a help in corrective speech or music training Thirdly, it is a universal phonetic pattern for the sound in which the characters always represent the same sound irrespective of the reader

The sound trace produced by the phonodeik appears complicated With the introduction of the oscilloscope, which reveals far greater detail, the complexity of speech sounds becomes even more apparent Various types of analysers have been applied to unravel these sound patterns The analysis consists essentially of breaking the particular sound into its component frequencies and expressing quantitatively their separate intensities, damping and duration Until recently this has been a most laborious process, so difficult that only short bits of the simplest speech sounds, the extended vowel, could be successfully handled

The spectra of such sounds are of the general form illustrated in *Figure 1* This is for the sound *o* in *Joe* in which the abscissa is frequency and the ordinate gives relative amplitude of each included frequency The analysis[3] for each of the ten spectra covers a time of speech of approximately one seventeenth of the one tenth second required for this sound in speech The number on the left of the diagram locates the spectrum in the time sequence of the complete sound The rapid variations in the component frequencies and also the two (or three) prominent regions in the neighbourhood of 400, 1,500 and 3,000 vibrations per second should be noted These intensity 'hills' of the vowel sounds will be referred to later

One may readily imagine from this analysis the intricate pattern associated with a sentence of speech The solid model in the lower portion of *Figure 2* is constructed from 200 oscilloscope traces for the words *visual telephony for the deaf* These 200 overlapping frequency band oscillograms were cut out in profile and stacked side by side In this model time advances to the right and the amplitude contribution of each frequency band is elevation in the rough topography of the model Such a spectrum may be compared to a light spectrum in which the chemical composition of the source undergoes a continuous change

PRODUCTION OF ORAL SOUNDS

The complexity of speech sounds is evident when we consider, even briefly, the sources and the modulating

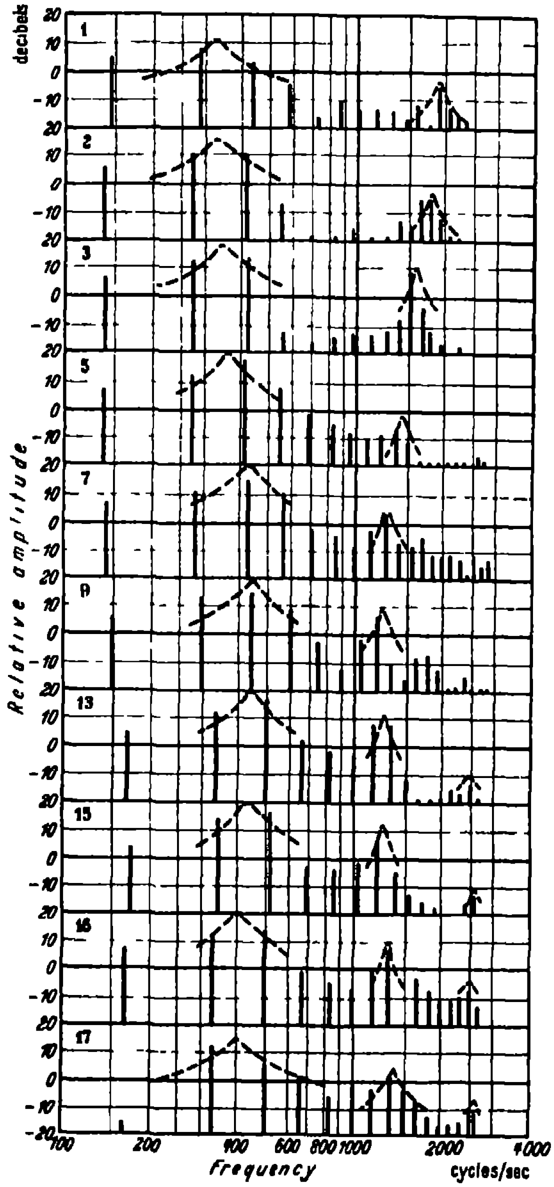


Figure 1 Analysis of successive periods of ' o ' in ' Joe ' (after J C Steinberg[3])

forces which operate to produce them The compressed air in the lungs is released in a series of starts and stops, pauses in the flow of speech These pauses are produced by the muscles of respiration, and the oral cavity closures, vocal bands, tongue, teeth and lips The pauses occur at a relatively slow rate and are inherent factors of syllabic speech The sudden starting and stopping of the air stream may be particularly noticed in such whispered or spoken words as *put* in which the initial and final sounds are sudden releases of air These may be either starts or stops and are designated as plosive sounds

Under proper tension of the vocal bands the air flow between them may set up vibrations to render the air stream audible This gives rise to voiced sounds of a general harmonic series particularly in the sustained vowel sounds The reader will note this harmonic content as he experiments on these sounds He will also note that the basic pattern varies in pitch for the several vowels

For many parts of speech the air stream is forced to flow through constrictions produced by parts of the oral cavity Try the word *see* and locate the source of the initial sound Under this friction condition the flow becomes turbulent, eddy whirls form, and the stream is modulated by a host of inharmonic components such as those characterized by hiss sounds in general

The frequency components, whatever their source, superimposed on the breath stream are themselves modulated by resonance in the oral cavities This is called cavity modulation Since the cavity form is continuously changing in speech by movement of the articulators teeth tongue *etc* a continuous change of frequency modulation takes place

The sound pattern of *Figure 2* for the words *visual telephony for the deaf* is so complicated that reading the words hidden in its detail appears impossible It must be remembered, however, that this is only a visual presentation of the same energy which falling upon the ear is translated with the speed of speech We follow also, without too great difficulty, different dialects which introduce variation in tonal components, pronunciation, inflection *etc* Likewise, studies show that spoken speech may be satisfactorily followed under conditions where only seventy five per cent of the syllables are correctly heard It therefore appears that our oral interpretation of speech depends only on certain major details of the speech track Evidently the balance lends some ease of understanding but, primarily, audible attractiveness or the lack of it do not detract

What are these essential elements which we may assume also as necessary in visible speech reading? How can they be best portrayed? A large number of studies have been made to find answers to these questions One of the most active centres in the United States is at the Bell Telephone Laboratory where these problems have been under review for a score of years A series of articles[4] from this laboratory and elsewhere has been published[5]

These reports show that visual reading of speech sound tracks is possible when the major frequency

Figure 2 A solid model built up of oscillograms for 200 overlapping frequency bands The words are 'visual telephony for the deaf' The two models differ in the amount of amplitude compression (after W Koenig et alii[8])

intensity changes only are presented A sample of such track is shown in the top portion of *Figure 2* in which the minor changes have been compressed Individuals with hearing, but not specifically selected for extraordinary ability, can learn to read a form of such simplified pattern for a vocabulary of a few thousand words at the rate of slow speech after a training period of three hours per day for six or seven weeks In the same time a congenitally deaf man learned to read a vocabulary of 500 of the most commonly used words

SOUND TRANSLATORS

Solid models of speech sound tracks would not be practical An advancement in this work was made with the introduction of the magnetic sound spectrograph[8] shown schematically in *Figure 3* This apparatus produces a two dimensional picture of the sound field with intensity as shades of grey or black Here the sound to be analysed is recorded on the loop of magnetic tape After recording, the reproducing element picks up the record and sends it to a frequency analyser set to transmit only a given frequency The contribution at this frequency is recorded on a single turn of the chart drum and corresponds to one trace of the hills of the model On the next revolution of both tape and drum the analyser is set to transmit a slightly higher frequency to record its contribution as variable regions of blackness next to the first trace The process is repeated for the full frequency range giving a pattern in which the topography has its hill crests in black shading to white in the valley or silent regions This is a form of representation which is readable and indicates that it is worth while to continue effort in this field which is now called Visible Speech, for its practical value alone A full description of the technical details, circuits *etc* of the spectrograph and the translators, to be described later, may be found in the reference articles

The desired goal of visible speech is not achieved if the pattern must first be slowly set up in reading form A transcriber must be perfected capable of producing the pattern of these major elements of speech immediately as they are spoken Two methods appear possible First, there may be a whole battery of analysers, simultaneously in operation, each taking care of its frequency portion of the composite track Secondly, there may be some extremely rapid scanning device by which the track can be repeatedly covered in a time interval which is short compared to the fluctuations of the important speech elements Difficulties are foreseen in either method when the range of frequencies in speech and its rapid fluctuations are taken into consideration

Recent investigations show that frequency differentiation, however, need not be sharp for the pattern

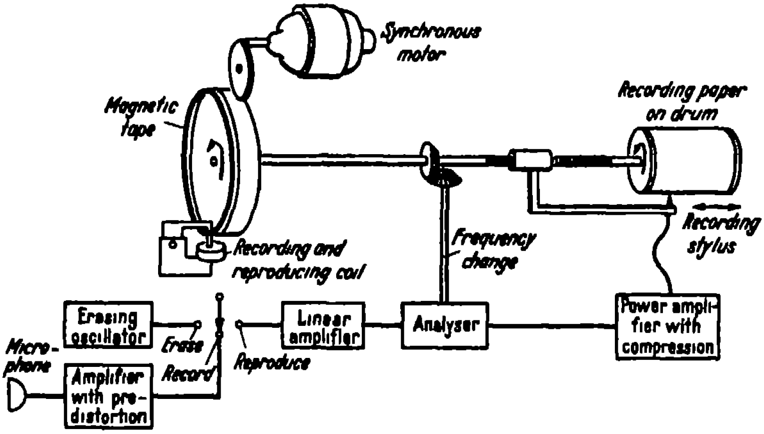


Figure 3 Schematic representation of the basic method of the sound spectrograph (after W Koenig et alii[8])

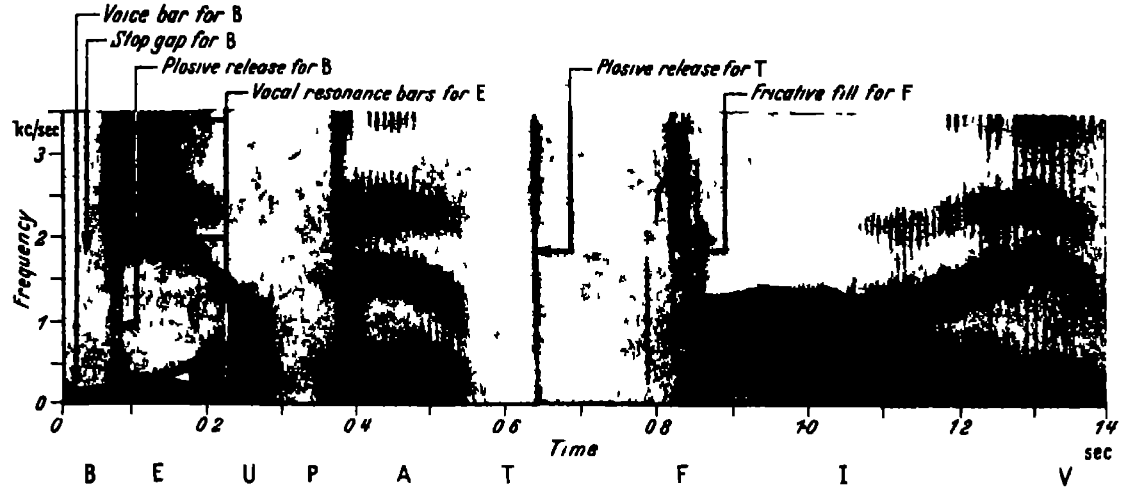


Figure 4 Spectrogram of the words ' be up at five' (after J C Steinberg and N R French)

to be readable A record expressed as the contributions of as few as twelve contiguous frequency bands of 300 c/s each extending to 3,600 vib/sec gives sufficient detail This means that only a dozen frequency band analysers need be available to produce the continuous visible track as the words are spoken

Figure 4 represents a typical pattern produced by one of the more recently designed translators meeting these specifications It is visible speech for the words *be up at five'* The abscissa is time and the ordinate shows the contributions of energy in the several frequency bands, with the low frequencies at the bottom increasing to the 3,300 to 3 600 vib/sec band at the top The blank spaces or stop gaps for the sounds *b*, *p* and *t* are produced by closures made in speaking the stop consonants The bar on the baseline of the stop gap for *b* shows that the sound is voiced The plosive releases appear as narrow irregularly striated regions extending the length of the vertical dimension The broad dark bands or bars indicate vocal resonances They curve from the resonances characteristic of one sound to those characteristic of a following sound Here is a sound alphabet which all readers translate essentially into the same sounds, even though it be an unknown language This track will be examined later

Several types of continuous analysers were constructed ten or more years ago to locate the prominent frequency regions in sounds These have followed both the principle of rapid scanning and of a set of fixed frequency band analysers in continuous operation Each, however, was so decidedly limited in the completeness of operation as to be totally inadequate to fill the present need Two recently constructed devices represent a closer approach and will be described

The phosphor belt translator shown in the block circuit of *Figure 5* is of simple construction The speech sounds are passed into a set of 12 band pass filters Each of these filters transmits the energy of its selected band of frequencies having a width of about 300 vib/sec and centred 300 vibrations apart This covers the range to 3,600 vib/sec Each filter is attached, through an appropriate circuit, to an individual grain-of-wheat lamp placed just above a phosphor coated belt The lowest frequency filter energy excites the bottom lamp and, if of sufficient intensity, impresses a light track on the belt The other filters, of increasing frequency range, act on their lamps placed in order so that the top lamp is excited by the highest frequency components of the sound The belt moves slowly across the field of view carrying the phosphorescent pattern produced by the flashing light of the lamps The decay time of the image allows a number of words to be visible at one time These are replaced by the new sound pattern as that portion of the belt starts on its next circuit

The cathode ray translator of *Figure 6* is a more complicated unit It uses a revolving cathode ray tube as a screen The sound is again passed into a set of twelve band pass filters covering the required range These band outputs are impressed in turn on the intensity control grid of the cathode ray tube as the beam sweeps vertically across the field On each trip the low frequency pass filter excites the beam on the bottom end of the swing, the highest frequency

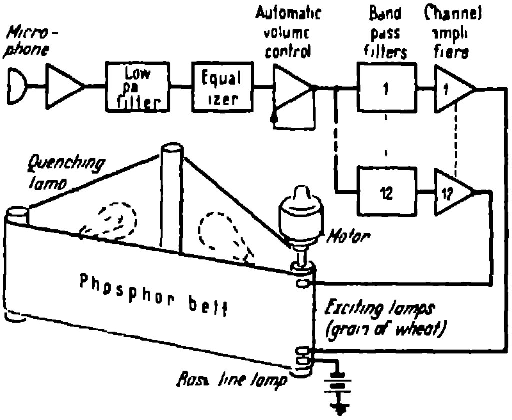


Figure 5 Block circuit of the phosphor belt translator (after H Dudley and O O Gruenz Jr[8])

at the top and the others likewise at their selected positions The tube is rotated slowly on a vertical axis so that each trip of the beam traces its pattern beside the preceding one Since the screen retains the image for about two seconds the pattern can again be scanned in word units

What are some of the associated patterns for the essential speech characters in this method of presentation which must be learned by the person wishing to read them? As stated earlier, certain unique characteristics classify common groups of sounds and form keys which make it unnecessary to memorize the innumerable possible patterns of speech These are associated with their mode of production and serve as guides in translation The training, therefore, involves a study of the patterns correlating them into groups associated with their common mechanism of formation The learner is thus not left completely ignorant of the probable visible speech pattern of a still unseen word

INTERPRETATION OF VISIBLE SPEECH PATTERNS

This review must be restricted to a consideration of only a few of the major features which show the general ideas involved[10] These are set out individually in *Figure 7* which is included so that the reader may localize each type and note also the variations from these patterns as the sounds merge from one syllable into the next in the pattern of the track shown earlier for the words *be up at five*

Voice bar— This is a low frequency component characteristic of those sounds in which the vocal band vibration is modified by a closed cavity It is the initial voiced sound of the *b* in the word *be*, *Figure 4*, and is here followed by the sudden opening of lips to produce a plosive release

Resonance bars— The vowel sound *e* of *be* is produced by vocal band action in an open cavity and shows as a characteristic set of resonance bars Such energy hills are evident in the analysis shown in *Figure 1* Each vowel has its own bar number and position, but in general the bars change progressively from the front to the back vowel sounds There is a shift in the prominent frequency regions for these bars as the sounds proceed to the beginning of the next word This is even more evident in the comparison of *e* and the *a* following They emphasize harmonics at different parts of the frequency scale

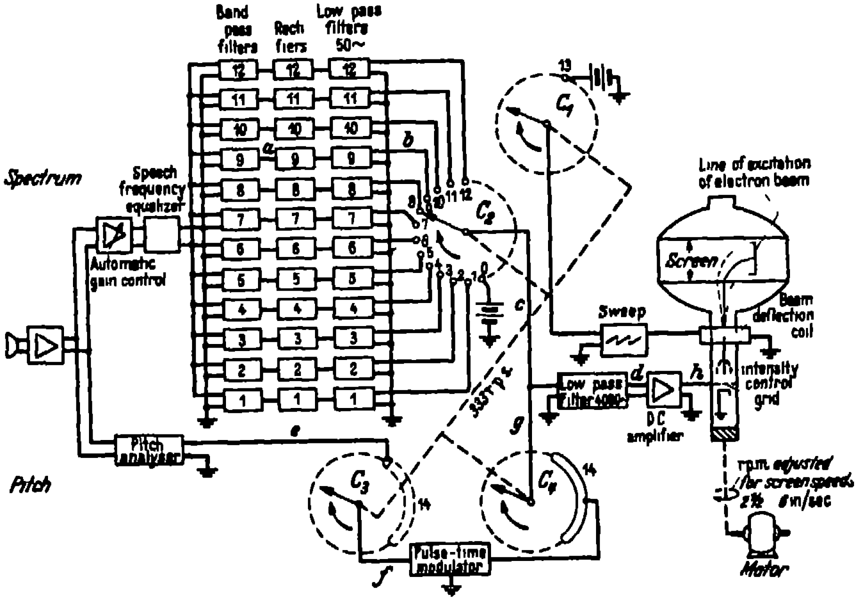
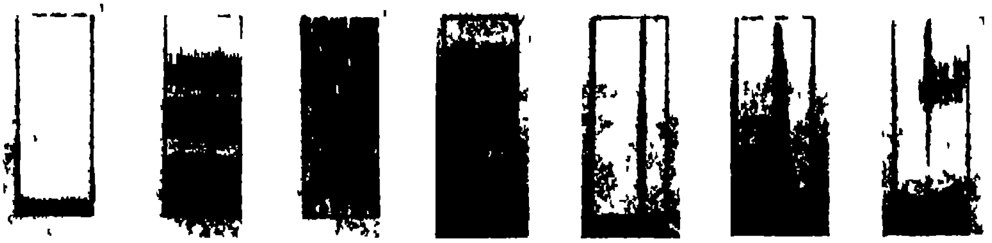


Figure 6 Schematic of cathode ray translator (after R R Riesz and L Schott[9])

Stop gap— In pronouncing the word *at* the reader will note a silent phase in the centre of this spoken word, seen also in the pattern Here the air stream

Figure 7 Visible patterns produced by various types of modulation (after G A Kopp and H C Green[10])



	a	b	c	d	e	f	g
Description terminology	*voice bar*	*resonance bar*	*fill*	*voiced fill*	*stop gap-glottal spike*	*stop gap spike fill*	*voiced stop gaps spike fill*
Modulation	*vocal cord closed cavity*	*vocal cord open cavity*	*frictional*	*vocal cord partially closed cavity frictional*	*stop-start*	*stop-start frictional*	*vocal cord stop-start closed cavity frictional*

is stopped momentarily, followed by a sudden frictional release of air This release for the *t* sound introduces the entire gamut of frequencies to produce the vertical spike showing contributions from all the frequency band analysers

Frictional fill and voiced fill— The *f* and *v* sounds of the word *five* are also largely or partially frictional The first part *f* in *five* is unvoiced The air stream blown through the constricted lips gives a sustained inharmonic of a large range of frequencies Not all sounds of this type, however, emphasize the entire band, nor are they produced in the same way, as is shown by the whispered words *he* and *she* It will be recognized that the first is stronger in the lower frequency region and would thus produce a fill in the bottom area of the pattern The last portion of the sound *five* is a composite of voiced and friction sounds The pattern of the vocal band vibration has been modified by a partially constricted oral cavity hindering the flow of the air stream

We recognize differences in the speech of individuals saying the same sentence To what extent does this modify the visible speech pattern ? *Figure 8* shows the variations and the similarities in the pattern of the same words *we are here* as spoken by four individuals of different phonetic treatment It is

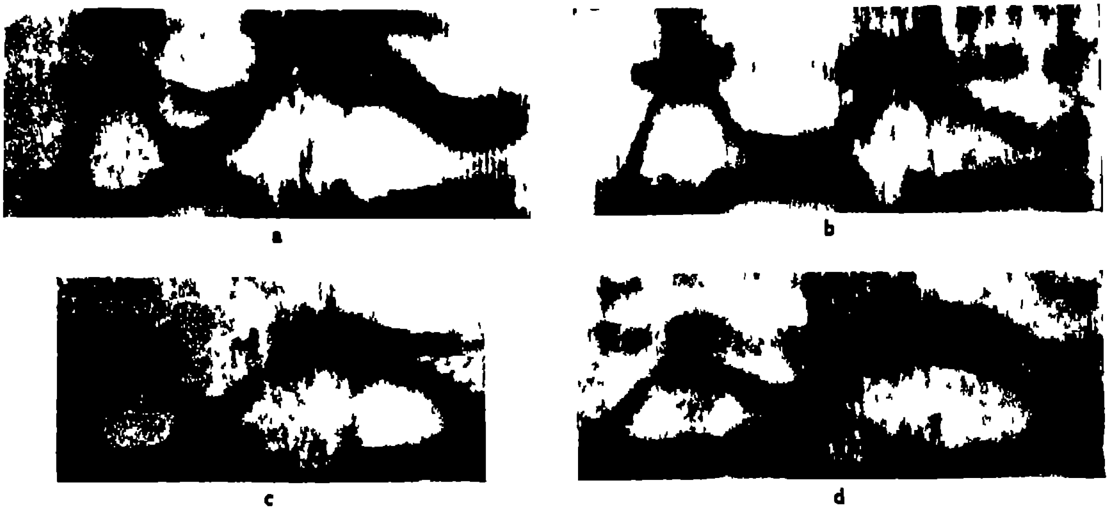


Figure 8 Illustration of sectional speech similarities and differences (after G A Kopp and H C Green[10])

a *We are here (General American)*
b *We are here (English)*
c *We-are here (Eastern)*
d *We are here (Southern)*

probably evident that these four speech tracks do not vary to any greater extent than the hand writing of the four individuals might vary and still be readable It is interesting to attempt to pick out the approximate division lines for these words *we are here* in the pattern Where would you locate the beginning sound of the third word ? The reader may wish to learn more[11] about this new field than is possible from this short and somewhat oversimplified version

FUTURE DEVELOPMENT

It is uncertain to what extent this field of sound writing and reading may develop It is still in its growing stage and there is a possibility that a better means of portraying the pattern for easy reading may be devised Various ideas are being extended[12] One of the present projects is concerned with a means of showing more vividly the intensity changes in speech A form of colour presentation is receiving attention Other investigators are working on the essential pitch changes which occur in speech and on a method of recording them Some type of contour pattern may be the answer The journals of acoustics carry many papers in this field

There is a definite need for this development and the initial tests show that the possibility of supplying the want is good Engineering skill and the new tools of science may eventually perfect portable translators within reach of the consumer's purse This has not been achieved, but it is the most hopeful new avenue for communication with individuals of extreme hearing loss

A vivid imagination may even suggest to the reader the possibility that some day our printed material may be directly sound transcribed into a universal form of sound writing and reading

The writer expresses his thanks to the authors of the diagrams in this paper, to the Bell Telephone Company and to the Journal of the Acoustical Society of America for permission to use illustrations

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Laboratories of the Carlsberg Foundation

H HOLTER, Dr Phil

Head of Cytochemical Department

CARLSBERG LABORATORY

The Carlsberg Laboratory was founded in 1875 by the Danish brewer J C Jacobsen, and its support is one of the various scientific activities of the Carlsberg Foundation Financially these activities are based on the income of the Carlsberg Breweries which after the death of the founder (1887) became the property of the foundation, and which have since been administered by a purely scientific board of directors, elected by the Danish Academy of Science

The two original departments of chemistry and physiology still form the backbone of the Laboratory, but the rules of the institution are elastic enough to permit the establishment of more or less temporary sub-departments dedicated to the pursuit of a more specialized line of work, such as yeast physiology and cytochemistry

The Carlsberg Laboratory, although independent of the government and not connected with the university or other educational institutions, accommodates many visiting scientists, both from Denmark and abroad, who come to be trained in one or another of the research techniques the development of which has been a speciality of the laboratory ever since

J KJELDAHL in 1878 created his famous method for the determination of nitrogen

Chemistry and biochemistry—The activities of the chemical department under its present director, K LINDERSTRØM-LANG (director since 1938), are in many respects related to the work of his predecessors, J KJELDAHL and S P L SØRENSEN, who were both interested in the chemistry of proteins and of enzymes

One of the problems studied in the chemical department is the mechanism of the initial phase in the enzymatic breakdown of proteins, and its relation to the process of denaturation The question is whether proteins are attacked by the same enzymes that are able to split peptide bonds in simpler peptide chains This seemingly simple question may well be complicated by the possibility that the true splitting of peptide bonds is preceded by the denaturation of the protein These problems are being studied by means of a close investigation of the tryptic breakdown of β-lactoglobulin, a crystalline protein which is the subject of numerous earlier publications from the department

Of the various techniques utilized in these studies one should be mentioned, namely the dilatometric determination[1] of the contraction which accompanies the enzymatic breakdown of proteins This contraction is abnormally large during the initial stages of the tryptic breakdown of lactoglobulin This is interpreted as pertaining to a denaturation process that precedes the true proteolytic action and which is likewise catalysed by the enzyme[2] Similar volume effects are observed in other, but not in all, protein-substrate systems, and interesting conclusions may be drawn regarding both the mechanism of proteolysis and the structural pattern of the proteins concerned[3]

Another problem being investigated is the formation of a new crystalline protein, plakalbumin, from ovalbumin[4], by a reaction catalysed by an enzyme from *Bacillus subtilis* The nature of this process and the composition of the products (simple peptides) are being investigated, using among other techniques an osmometer measuring the osmotic pressure of protein solutions with an accuracy of one to two per cent[5]

Various other problems pertaining more or less closely to protein chemistry which are being investigated include the possible role of certain phosphoric acid derivatives in the synthesis of peptide bonds[6], the reaction of carbon disulphide with amino acids, peptides and proteins[7], the breakdown of ribonucleic acid by ribonuclease[8], the peptidase activity of human serum and of haemolysate[9]

Histochemistry—In the thirties, in collaboration with K LINDERSTRØM-LANG, the author initiated a series of investigations on the subject of enzymatic histochemistry The immediate aim was the quantitative determination of tissue enzymes on a very small scale, so that the samples investigated could still be subjected to a quantitative histological analysis, in order to permit a topographical survey of enzyme distribution

In the development of the micromethods which were indispensable for this purpose a common principle was followed, which was to reduce volumes and amounts rather than to attain the necessary reduction of quantities by very high dilutions and by the employment of very specific and sensitive reactions Thus the basis of the methods (reviewed by D GLICK[10]) is a system of micropipettes and microburettes adapted to working with microlitres instead of millilitres of reagents, substrates *etc* Various hydrolytic enzymes are thus determined by means of suitable titrimetric methods on a microlitre scale

For the determination of respiratory enzymes another tool has been devised, the Cartesian diver microrespirometer[11] It is based on the principle that any change in the amount of gas in the diver requires a change in the pressure necessary to keep the diver floating A pressure reading with an accuracy of 1 mm of water will measure the amount of gas in the diver with an accuracy of 1×10^{-5} µl The Cartesian diver has been used for measurements of respiration and respiratory enzymes in various objects and also for numerous other analytical applications *e g* the determination of cholinesterase, aneurine, cystine *etc*[12]

Another principle that was adapted to histochemical purposes is that of dilatometry, comprising basically a tube containing a density gradient in a non-aqueous medium in which a small drop of less than one microlitre of aqueous reaction mixture is suspended Changes in volume of the drop due to certain chemical reactions cause a displacement to a new level of density equilibrium Since the position of the drop can be measured with an accuracy corresponding to 1×10^{-6} in the density determination, this is a very sensitive method of measuring reaction rates in exceedingly small samples It has been used for the determination of peptidase activity and, naturally, for many measurements of specific gravity, including the determination of heavy water[13]

The histological samples investigated by the various methods here described are microtome slices cut from frozen tissues Such slices were used both for the measurement of enzyme content and for histological control

These techniques have been applied to studies[14] on the distribution of proteolytic enzymes, lipase, cholinesterase and urease in the glands of the stomach mucosa, and to the study of the distribution of amylase and peptidase in the tissues of sprouting malt

Cytochemistry – The histochemical studies described above naturally led to work on a cytochemical scale, where one was no longer primarily concerned with the enzymatic constitution of tissues, but rather with that of the cell itself *i e* with the various constituents of cytoplasm This expanding line of research led in 1943 to the establishment of a sub-department of cytochemistry under H Holter

The work of this department is essentially based on the same methods as the histochemical investigations, the only difference being that the objects investigated are still smaller and that some of the methods therefore had to be made still more sensitive This requirement led to the development, by E Zeuthen[15], of a 0 1 µl diver with a sensitivity of 2×10^{-6} µl Another development of the Cartesian diver principle[16] is the diver balance which permits the determination of the mass of biological objects with an accuracy of 1×10^{-3} µg The great technical progress of recent years with regard to spectrophotometry and photoelectric colorimetry has also made possible the development of some microcolorimetric methods which allow the measurement of extinction in µl samples[17]

The main objects of the studies on the chemistry and physiology of the cell using these techniques are amoebae and egg cells of aquatic organisms Often the cell constituents are arranged in layers according to their specific gravity by means of Harvey's microscope centrifuge which permits the optical control of the cell during centrifugation When the desired degree of stratification has been reached, the cytoplasmic layers are separated by means of microneedles The enzyme content, respiratory activity *etc* of the cell fragments are then determined and compared with the relative amounts of cytoplasmic constituents

One of the fundamental difficulties in this type of work is to find suitable magnitudes of reference It is usually fairly easy to determine the total respiration or the total content of some enzyme in a given cell or cell fragment, but that does not mean much unless it can be expressed as activity per weight or volume or nitrogen content *etc* Sometimes this difficulty can be overcome by counting the number of objects like cells, nuclei, or food vacuoles, but often some direct means of measurement is indispensable and to meet this need methods like the diver balance, a colorimetric volume determination, or a nitrogen determination on a 10^{-1} µg scale, had to be devised

The problems studied in this way include cytoplasmic and metabolic changes during starvation of amoebae[18], distribution of proteinase, peptidase and amylase in amoeba cytoplasm[19], studies on the supposed metabolic gradient of echinoderm and ascidian eggs[20], oxygen uptake during mitosis[21], peptidase content of lymphocytes[22], and digestion of food in amoebae, studied by means of radioactive carbon[23]

Plant physiology— An independent line of investigation is pursued by C Olsen in his work on the mineral plant nutrients and especially on the uptake and exchange of ions by the higher green plants He has recently shown (unpublished) that, contrary to current opinion, the uptake of ions like Ca, Mg, nitrate phosphate and sulphate is within wide limits independent of the concentration of the respective salts in the culture solution In other words, the limiting factor for the rate of uptake is the active expenditure of energy by the plant The picture is sometimes complicated by the phenomenon of ion antagonism, but even then the molar sum of cations or anions taken up is independent of concentration Earlier studies from recent years include seasonal changes in mineral and other nutrients contained in beech leaves, the manner of fixation of potassium in beech leaf cytoplasm, and problems of calcium uptake in plants growing on calcareous soil[24]

Physiology— Since 1933 the physiological department has been directed by the geneticist Ø Winge, who once more made yeast the main object of the department's activities

The first and probably the most important step in the recent sequence of yeast studies was the discovery in 1935 of a regular alternation between a haplophase and a diplophase in the life cycle of yeast[25] This discovery not only established the existence of alternating generations, just as in other plants, but it also opened up the possibility of demonstrating in yeast the same genetic phenomena that have been demonstrated in higher plants and animals Especially significant in this respect was the discovery 1 that even a culture originating from a single cell can be segregated in different types if the spores from an ascus are isolated by means of a micromanipulator and are cultivated separately and 2 that hybrids can be obtained by inducing two haploid spores from different yeasts to copulate and thus form a diploid zygote from which the hybrid yeast develops[26] This is accomplished by placing the two spores together in a very small droplet in a sterile operation chamber Besides giving access to more detailed genetic studies, this method opened the way for practical improvement of yeasts by the well established methods of plant breeding, namely, hybridization and subsequent selection

To these tools was added the evaluation of the macroscopic appearance of giant colonies growing on a solid wort gelatin surface Each culture is characteristic of the individual biotype, showing a structure which can be interpreted as the expression of a primitive organization, *Figure 1*

The giant cultures shown in *Figure 1* are very valuable in the demonstration and identification of hybrids, but still more so for the study of mutations This is clearly demonstrated by the schematical *Figure 2*

The mutants shown in *Figure 2* which have arisen during the growth of the giant culture form sectors the shapes of which are determined by the capacity of the mutants to compete with the mother type Sectors *a* and *b* represent mutants which were incapable of competition, and were therefore suppressed during the growth of the giant colony Mutant *e* has been able to assert itself better, still, its convex border lines testify to its inferiority Mutant *c* appears to be more vigorous, its demarcation from the mother type is represented by straight lines Mutant *d* shows a still more vigorous growth, it not only increases in width at the expense of the mother type, so that the border lines have become concave, but at the margin of the colony it even projects on account of its more rapid growth Mutant *f* has arisen later than the others, which have been present in the inoculate or appeared shortly after the inoculation, judging from the form of the sector it seems to be a type capable of competition

On the basis of these methods and discoveries a series of investigations on the genetics and physiology of various yeasts has been and is being conducted Problems of segregation and mutation have been studied[6,7] with the result that the saccharomycetes must be regarded as very labile organisms, so far every culture examined has shown numerous mutations on standing for some months or years This presents practical difficulties in investigations which involve protracted experiments, as only short time experiments offer a fair chance that mutations will not take place during the experiment itself

Special interest attaches to the recent investigation[18] of the inheritance of enzymatic characters in yeasts, and the phenomenon of enzymatic adaptation which plays such an important role in the practice of microbiology Closely connected with the adaptation problem is the study of cytoplasmic inheritance[19] since this hypothesis has been used to explain some of the adaptation phenomena In the field of yeast physiology there ought to be mentioned a series of papers on the growth action of pantothenic acid, β-alanine, and their antagonists[20], and on the anti-vitamin effect of sulphanilamide and related substances[21].

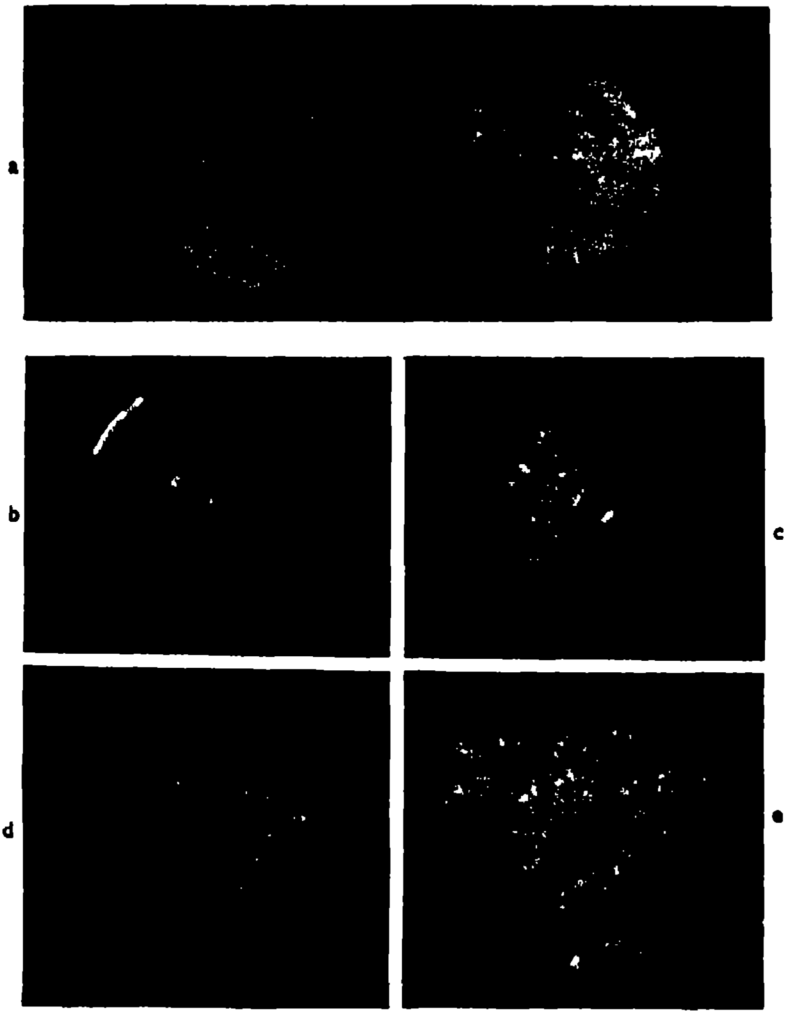

Figure 1 Giant colonies of yeast types (Saccharomyces), a *two giant colonies of* S cerevisiae Hansen Rasse II, *28 days old,* × *3* b–e *different types segregated from* S cerevisiae Rasse II *through single spore culture, 29 days old,* × *3*

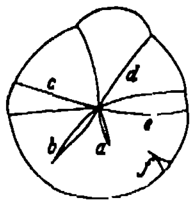

Figure 2 Different types of mutant sectors in yeast colonies

Other recent studies include an investigation on artificial hybrids between salmon and trout[32], and cytogenetical studies on the taxonomy and evolution of *Frophila*[33], and on chromosome numbers in the *Malvaceae*[34]

BIOLOGICAL INSTITUTE OF THE CARLSBERG FOUNDATION

Both in scope and organization this institute is independent of the Carlsberg Laboratory In recent years the main activities of the institute have been centred on two problems *1* the pathogenesis of cancer, studied mainly by an investigation of the properties of cancer tissue grown *in vitro*, *2* a study of the nature of the growth promoting substances from embryonic tissues Attempts towards purification of the high molecular growth substances seemed to indicate that they behaved like nucleoproteins[35] While these attempts were only partially successful, they gave rise to a closely related line of work which is most actively pursued at present and which shows great promise This concerns the action of low molecular substances ('accessory growth factors') especially the amino acids[36] Technically, the essential point in these investigations is that the culture media (plasma, serum, embryo extract) are dialysed before use The substances thus removed may then be added one by one and their importance for the growth of the tissue culture may be studied[37]

These experiments showed that dialysis leads to a state of deficiency in which cell life cannot be maintained Among the substances able to remedy this deficiency, at least partially, were a mixture of amino acids, glutamine, glutathione, fructose diphosphate, glucose, and a number of salts If these substances are added to the dialysed blood plasma it is possible to cultivate heart fibroblasts for at least ten passages A partially synthetic medium has thus been devised[38]

There are of course still many unknown substances present in the dialysates from natural media So far, there have been found among others ethanolamine phosphate carnosine, cysteic acid, and a number of peptides[39]

It is to be hoped that this line of attack will lead to a still more detailed elucidation of the nutritive requirements of tissue cells At present, the work on the culture of malignant tissues, which had been suspended for some years, is being resumed with the aim of comparing the nutrition physiology of normal and malignant cells

Originating in the investigations on tissue culture several side lines have been taken up These include the mechanism of blood clotting[40], antithrombin[41] and the synthetic anticoagulants[42] For the present the interest has centred about the proteolytic (fibrinolytic) enzymes present in blood, and it was found that they could be activated by means of an activator present in the tissue cells[43] Studies on the fractionation of proteins by means of specific anionic and cationic precipitants are being conducted[44], and the interest in low molecular accessory growth substances has led to investigations on enzymatic processes occurring in tissue extracts, especially those related to nitrogen metabolism

MARINE BIOLOGICAL LABORATORY

J Schmidt, who directed the physiological department of the Carlsberg Laboratory until 1933, was deeply interested in the exploration of the ocean He led the 'Dana' oceanographical expedition round the world in 1928-30 and on his death in 1933 the Marine Biological Laboratory was set up to take care of his collections These include mainly pelagic animals from all oceans, some have been distributed, especially among foreign collaborators, while much has been maintained at the Marine Biological Laboratory itself Most of the results are being treated in the *Dana Reports*, published by the Carlsberg Foundation To date, six volumes containing thirty four papers have been issued in the series

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Miscellaneous Notes

ROYAL SOCIETY

AT a recent meeting the following were elected Foreign Members of the Society Dr W S ADAMS (Pasadena), Professor C F CORI (St Louis), Professor E FERMI (Chicago), and Professor C J F SKOTTSBERG (Gothenburg)

During the Royal Society Scientific Information Conference and in the work of the Information Services Committee since it has been evident that a list of United Kingdom scientific journals publishing a substantial proportion of original work or critical reviews would be useful to many members of the scientific community Such a list has now been prepared* News journals have been omitted and only a few of the chief commercially sponsored journals and the publications of Government departments have been included Each entry includes a short description of the contents of the journal and any indexes, its frequency of issue, the current volume number, approximate size, whether summaries of papers are given, where and how directions to authors may be obtained, price, address of the editor and of the publishing organization The main list is in alphabetical order of the names of the Society or organization but there are indexes of names of journals and subjects All scientific workers whether in pure or applied fields should find this book very useful indeed

UNIVERSITY APPOINTMENTS

London— Professor H S W MASSEY, F R S, Goldsmid Professor of Mathematics at University College, has been appointed to the Quain Chair of Physics tenable at the College from 1 October 1950

Professor R W RUSSELL has been appointed to the University Chair of Psychology tenable at University College from 1 October 1950

The title of Professor of Mining Geology in the University has been conferred on Dr D WILLIAMS in respect of the post held by him at the Imperial College of Science and Technology

Dr D H R BARTON has been appointed to the University Readership in Organic Chemistry tenable at Birkbeck College from 1 October 1950

The title of Reader in Chemistry in the University has been conferred on Dr A G FOSTER in respect of the post held by him at Royal Holloway College from 1 October 1950

Dr D M A LEGGETT has been appointed to the University Readership in Mathematics tenable at King's College from 1 October 1950

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* *A List of British Scientific Publications Reporting Original Work or Critical Reviews* (94 pp) London Cambridge University Press for the Royal Society, 2s 6d

ELECTION OF OFFICERS

Royal Institute of Chemistry— Among the officers elected for the ensuing year are President, Professor J W Cook, F R S , Vice-Presidents, Professor F Challenger, Professor H Krall, Professor W H Linnell, Professor R P Linstead, C B E , F R S , Dr G Roche Lynch, O B E , E T Osborne, O B E , Honorary Treasurer, Dr D W Kent-Jones

British Tar Confederation— The following have been elected for the year 1950 President, Colonel H C Smith, O B E , D L , Honorary Treasurer, C E Carey , Chairman of the Executive Board, W K Hutchinson , Vice-Chairmen of the Executive Board, Sir Walter Benton Jones, Bart and Major A G Saunders

Institution of Chemical Engineers— The following are among the officers elected for the ensuing year President, Professor D M Newitt , Vice-Presidents, M B Donald, Dr F A Freeth, A L Leighton, J A Oriel, C B E , Honorary Secretary, L O Newton , Honorary Treasurer, F A Greene

Institute of Petroleum— Elections for the year 1950–51 include President, C A P Southwell , Vice-Presidents, M A L Banks, E J Dunstan, Dr F Morton, J S Parker, H C Tett , Honorary Secretary, C Chilvers , Honorary Treasurer, G H Coxon

REITH LECTURES 1950

The B B C announces that this year's Reith Lectures will be given by Professor J Z Young, F R S , Professor of Anatomy, University College, London, on the subject of Doubt and Certainty in Science The lectures will be broadcast in the autumn in the Home Service with repeats in other programmes

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

Professor Sir Ian Heilbron, D S O , F R S , has been appointed Chairman of the Advisory Council for Scientific and Industrial Research in place of Sir Geoffrey Heyworth, who has resigned

Professor W J Pugh, O B E , Professor of Geology and Deputy Vice-Chancellor in the Victoria University of Manchester, has been appointed to be Director of the Geological Survey and Museum of Practical Geology He will succeed the present Director, Dr W F P McLintock, in the autumn of 1950

BRITISH IRON AND STEEL RESEARCH ASSOCIATION

Constitution of Alloys Group— A group has been set up to undertake the coordination of phase diagram work being carried out in connection with metallurgical subjects, especially the transitional elements and high temperature alloys The chairman is Professor G V Raynor and its members are R L Bickerton, Dr A J Bradley, F R S , Dr A M B Douglas, Dr G A Geach, H J Goldschmidt, Dr J L Haughton, Dr W Hume-Rothery, F R S , H W L Phillips, Dr A G Quarrell, Dr T Raine, W P Rees, Dr A H Sully, and Dr H Sutton

International Research on Flame Radiation— France, Holland and Great Britain are cooperating in an investigation of the factors affecting luminous flame radiation, using an experimental furnace in the Royal Dutch Steelworks, Ijmuiden

Both ' engineering ' and ' scientific ' trials have been agreed upon In the former a large number of independent variables such as fuel rate, kind of fuel, kind of burner, excess air ratio *etc* is studied In the more fundamental trials, which are expected ultimately to lead to results at least as practical as the more empirical engineering ones, a relatively small number of different flame settings is to be studied in great detail

Chairmen of committees for each country are Professor G M Ribaud (France), J E de Graaf (Holland) and Professor O A Saunders (Great Britain) M W Thring is in charge of the research programme

New Research Station— A new type of research station which will have much of the equipment of a steelworks in miniature is to be begun in Sheffield during the next few months Pilot steelworks plant for melting, rolling, drawing and forging, to try out research results before application to production plant, is to be installed

Steel melting will be carried out in a 10 cwt (500 kg) capacity electric arc furnace, which will be used for work on sulphur elimination and on problems of electric furnace practice

A high speed 14 in (35 cm) four-high cold strip rolling mill will enable investigations to be carried out into such things as ' roll force ', the measurement of which gives rolling mill makers and users the equivalent of the boiler engineer's steam pressure gauge in working out safe and economical loads On a smaller two-high mill valuable work has already been done by the B I S R A 's rolling section but there must now be larger, fully instrumented, equipment, more akin to modern industrial practice, on which to take this work further

B I S R A will have its own experimental wire drawing plant in the new buildings, where it will be possible to carry out trials of new processes before they go on to the full scale production plant

NATIONAL RESEARCH COUNCIL, CANADA

Dr E G YOUNG, Professor of Biochemistry, Dalhousie University, has been appointed Director of the Maritime Regional Laboratory at Halifax, Nova Scotia.

Building Research— One of the most important projects recently initiated by the soil mechanics section of the Division of Building Research deals with settlements of the foundations of large buildings. In several Canadian cities, foundation soils consist of clays which are highly shrinkable or compressible under the superimposed load of buildings. This reduction in volume of soils may produce differential settlement in the buildings either by variations in the foundation soil or by uneven loading, thus in many parts of the building structural stresses may become greater than those provided for in the design, causing strain and consequent damage.

The first part of the project is concerned with determining the relevant characteristics of soils by means of consolidation tests. Eventually, when enough information on the soil in each area has been collected, it may become possible to predict such characteristics merely on the basis of routine soil tests. A two-unit consolidometer to test samples 2½ in (6.3 cm) in diameter is being built by the Division of Building Research from a design developed by the Hydro Electric Power Company of Ontario. The construction of apparatus accommodating larger samples will follow.

In the next phase of the project, theoretical calculations on subsidence of buildings, based on the results of consolidation tests, will be checked against the actual course of settlement.

Pure Chemistry. A detailed study of the factors which may affect the sorption of acid dyes by wool has been undertaken by the fibre chemistry section. Factors to be considered are: combination of hydrogen ions with wool, anion affinity, adsorption, and Donnan equilibrium effects, the latter necessitating an investigation into the swelling of wool under various conditions. The effect of temperature on the sorption of dye is also under study. Tests from room temperature to boiling point have been made at ten degree intervals for one concentration of acid.

In work on a new problem, the sorption of vapours and gases by wool, and sorption isotherms of hydrochloric acid gas at room temperature have been measured.

COMING EVENTS

International Symposium on Chloromycetin, 2nd Italian Congress on Antibiotics, Milan, 3–5 June
National Mechanical Handling Exhibition, Olympia, London, 6–17 June
Industrial Equipment and Engineering Fair, Nairobi, Kenya, 9–24 June
International Ornithological Congress, Uppsala, 10–17 June
33rd Canadian Chemical Conference and Exhibition, Royal York Hotel, Toronto, 19–22 June
International Conference on the Preparation of Coal, Centre d'Études et de Recherches des Charbonnages de France, Paris, 26 June–1 July
Conference on Physics of Lubrication, the University, Manchester, 29 June–1 July
13th Meeting of International Conference on Large Electric Systems, Paris, 29 June–8 July
Second Conference on Oil Shale and Cannel Coal, Royal Technical College, Glasgow, 3–7 July
Conference on Civil Engineering Problems in the Colonies, 1950, London, 3–7 July
Rockefeller Colloquium on Ferromagnetism and Antiferromagnetism, Faculté des Sciences de Grenoble, 3–7 July
International Colloquium of International Union of Biological Sciences on Rheological Problems in Biology, Stockholm, 7–10 July
Building Research Congress 1951, Watford, 11–20 September 1951

New Books

Sound Absorbing Materials

C ZWIKKER and C W KOSTEN

(x+174 pp, 92 illus, 9½ in by 6 in)

Amsterdam, Brussels, New York: Elsevier Publishing Co Inc, 1949 $3.00
London: Cleaver-Hume Press Ltd, 1949 22*s* 6*d* net

THIS book is not, as one might suspect from the title, a summary of acoustic characteristics of existing absorbing materials intended for practical applications in architectural work. It is, on the contrary, a highly scientific study of the physical behaviour of sound waves impinging on and penetrating into absorbent constructions of any type.

The first three chapters deal with the theory of sound absorption in porous and elastic media. The representation of the impedance curve in the complex plane is used to a large extent, thus giving a comprehensive conception of the acoustic behaviour of the material.

Chapter 4 refers to the experimental determination of the basic properties of sound absorbing media affecting their acoustical performance, that is to say porosity, air resistance, compression modulus and stiffness

In Chapter 5 the methods of measuring normal impedance and absorption are discussed whilst new procedures and apparatus developed by the authors and their collaborators as well as American practice are described The results of experiments are compared with theory in Chapter 6

The acoustical behaviour of resonators used a good deal in modern acoustical treatment are dealt with in detail in Chapter 7 Different types of perforated panels with various fillings of porous materials behind them are described and here some practical points of view are added

Most of the work laid down in the book is confined to normal incidence of sound, whereas in actual rooms a random distribution of angles of incidence occurs The last short chapter (8) is devoted to the oblique incidence of sound for special cases

Results mostly based on the assumption of normal incidence of sound cannot be expected to be in close agreement with the behaviour of the material under practical conditions In this respect, coefficients obtained by the reverberation method have a closer relationship to what is finally desired—in spite of all the deficiencies of the reverberation method

For readers however who are chiefly interested in the scientific aspect of the problem this book provides a very comprehensive treatise

O K Kolb

Das biologische Weltbild, I die Stellung des Lebens in Natur und Wissenschaft

L VON BERTALANFFY

(202 pp, 9½ in by 6½ in)

Bern A Francke A G Verlag, 1950 *S Fr* 11 00

As von Bertalanffy himself remarks the experimental observer is apt to have a horror of the theoretical scientist Yet there is much in this book to attract the experimenter It presents a so-called ‘ organic ’ view of living things as systems in a steady state with certain peculiar properties, especially that of self-regulation This is the picture of the organism that many observers are now building up for themselves, struggling, like von Bertalanffy, to fit them on to a science that is based on the comparison of the body with a machine, having ‘ structure ’ and ‘ functions ’

Unfortunately there is here, besides much that is stimulating, also all the apparatus of the ‘ theoretical scientist ’ The discovery of traces of each view in Greek thought, the quotations from Goethe, discussions of ‘ hierarchical organization ’, ‘ methodological concepts ’ and the like, that have driven many a good biologist away from paths he would like to follow Worst of all, there are severe symptoms of the besetting sin of the theorist– the taking too seriously of concepts that the experimentalist himself regards only as imperfect expressions of his observations We find painstaking analysis of the cell, the gene and many an other, all studied most carefully as they appear from analysis of the works of biologists

No doubt the exact person will throw up his hands and say ‘ what else is the poor reader to do ? How can he judge of the works of scientists except through their published words ? ’ And of course the exact one will be as right as he is prim Theoretical biology of this sort is extremely useful, but it will not win the heart of the working biologist until it shows its understanding of the anarchy of his method and the detached humour of his interest Who will bother to read all these long words when the beauty and excitement of the living things are there to be seen for themselves ?

J Z Young

Progress in the Theory of the Physical Properties of Glass

J M STEVELS

(xii + 104 pp, 26 illus, 8 in by 5½ in)

Amsterdam Elsevier Publishing Co Inc , 1948
London Cleaver-Hume Press Ltd, 1948 10s net

Much experimental work has been done during the past sixty or seventy years with the object of establishing relationships between physical properties and glass composition, but the various empirical expressions put forward have usually been applicable only to glasses of substantially similar types and over comparatively restricted ranges Dr Stevels's investigations have had little or nothing in common with this type of work which, however, has provided much of the factual information by which his theoretical deductions can be tested—and largely substantiated He begins with the type or types of molecular units necessary to build up a glass, and with the irregular network structure built up of the tetrahedral units characteristic of all glasses with the possible exception of boric oxide glass The modifications of structure due to the introduction of metallic oxides are then considered, and the ‘ housing ’ of the metallic atoms or ions within the structural interstices is also described From these Dr Stevels proceeds to discuss how the density will be affected by increasing the proportions of metallic oxides in relation to the ‘ glass-forming ’ oxides such as silica, and deduces generalized expressions which, to a first approximation, are independent of the nature of the constituent oxides Exceptions are numerous, but these are explained by unusual oxygen-silicon and oxygen-metal ratios, such as would invalidate the assumptions on which the theoretical treatment is based, and on the reasonably well established assumption that certain oxides can act partly as 'network builders' and partly as 'network modifiers' The electrical properties of glasses are dealt with on similarly fundamental grounds, as is also the molecular refraction of glass

There is a very large measure of agreement between the experimental values already obtained by previous workers and the values calculated by the author from his theoretical considerations where differences are found Dr Stevels can usually put forward good reasons for their existence His claims are commendably modest and show evidence of a sound critical faculty

To all who are interested in the physics and chemistry of glass, the monograph will be informative and stimulating It is by approaching the subject fundamentally, as here, that our knowledge of glass will be advanced most surely and most rapidly, and out of the differences found between experiment and theoretical prediction, new information will come and new lines of research be suggested

H MOORE

Frontiers in Chemistry, Vol VIII
Frontiers in Colloid Chemistry

Edited by R E BURK and O GRUMMITT

(*x + 157 pp, illus, 9 in by 6 in*)

New York Interscience Publishers, Inc, 1950 $4 00
London Interscience Publishers, Ltd, 1950 32s net

'FRONTIERS in Colloid Chemistry' is a series of lectures on adsorption, ion-exchange, sedimentation and colloidal electrolytes, by some of the most prominent American scientists These lectures were apparently delivered between 1946 and 1948 As a result of their belated appearance in print those lectures dealing with subjects which have since undergone rapid development can no longer be considered as an adequate representation of the subject This applies to H H STRAIN's discussion of 'Adsorption Analysis' and to R J MYERS' article on 'Ion Exchange and Synthetic Resins' subjects which have developed enormously during the last four years, both in theory and in experimental applications However, the excellent presentations by H S TAYLOR on 'Adsorption Isotherms', by V R DAMERELL on 'Sedimentation', by J W MCBAIN on 'Colloidal Electrolytes, Wetting Agents and Detergents' and on 'Organization of Crystals and Micelles of Soap', deal with subjects which had, at the time of their delivery, progressed to some state of completion They are, therefore, sufficiently fundamental in outlook and treatment to be of considerable value to the young student desiring to acquaint himself with the basic science of these fields This applies particularly to the lecture by DEAN TAYLOR which is of a more recent date It combines a lucid representation of the field with a more or less adequate documentation which introduces the student to many of the more detailed original papers

F GLUECKAUF

Photoelasticity, Vol II

M M FROCHT

(*xviii + 505 pp, 425 illus, 9 in by 6 in*)

New York John Wiley and Sons Inc, 1948 $10 00
London Chapman and Hall Ltd, 1948 80s net

VOLUME I of FROCHT's 'Photoelasticity', published in 1941, has been widely used as a textbook both by students and by technicians Its author is regarded as a leading expert in this field In Volume II he deals with the more advanced photoelastic and associated mathematical stress analysis, and includes a number of special investigations published by him since 1941

A whole chapter is given to the analysis of radial stress in a semi-infinite plate due to boundary loads, which shows remarkably good agreement between theory and experiment A further chapter deals with the stress in wedges due to tip pressures Here, again, theory and experiment provide convincing evidence of the reliability of the photoelastic method The use of the Airy stress function is illustrated by examples Considerable attention is paid to methods of determining isopachic stress patterns The interferometer method is illustrated by an interference fringe pattern for a stainless steel ring under diametral compression, the results of which are shown to agree with photoelastic measurements

Of recent years, the solution of Laplace's equation for '$P + Q$' (the sum of the principal stresses) by the iterative method has tended to replace the old lateral extensometer method The author gives a full description of the new method *ie* computing $P + Q$ by the harmonization of values established for a square network, using the boundary values given by the fringe pattern as a starting point Several examples are worked out and it is shown how, by using conformal transformation, problems involving circular holes or notches can be conveniently solved

Very useful to the designer are the curves for stress concentrations at a hole loaded through a pin in the hole, including the effect of clearance

Three chapters are devoted to application of the 'stress freezing' method for three dimensional stress problems, such as the stress distribution at holes in circular shafts, and a few examples are given of the method of oblique incidence Those chosen for analysis by the 'freezing' method are relatively simple stress distributions, and it is evident that the author does not consider the method easy to apply in its present form for *ad hoc* problems generally

An important discovery, from the point of view of accuracy, is that spurious edge stress in a thin slice produced in freezing *BT 61-893* (photoelastic bakelite, a glyptal polymer) disappears almost entirely within a few days due to redistribution of stress, provided the slice is protected from atmospheric moisture

The last chapter is devoted to the 'scattered light' method In the appendix, fringe photographs of slices from three dimensional models entirely free from spurious edge stress are shown These were obtained with the new photoelastic material known as *Fosterite*, which is said to be a generic name for copolymers of organic acids and diethylene glycol with styrene *Fosterite*, which appears to be ideal for three dimensional work, has been produced in bars of considerable thickness

As in the first volume, the author is not content with explaining a process of analysis, but gives one or more examples fully worked out Occasional problems are given as exercises for the reader The presentation, printing, and illustrations, as well as the paper, are excellent The text has evidently been checked with great care Though intended mainly for the advanced worker, this book should probably have a wider appeal than the classical treatise by Coker and Filon

W A P Fisher

Principles of Radar

D TAYLOR and G H WESTCOTT

(*x+141 pp, illus, 8½ in by 5½ in*)

London Cambridge University Press, 1948 12*s* 6*d* net

This book is one of a series of monographs dealing with advances in radio techniques made during the war It is accordingly a highly specialized work, but the authors have nevertheless succeeded in dealing with this branch of the subject in a manner which anyone with an elementary knowledge of conventional radio will find easy to follow At the same time the more advanced aspects of the subject are dealt with in sufficient detail, particularly in the Appendix, to interest the advanced worker

In the introduction there is a short historical account which will be of special interest to the reader who was not closely associated with radar development in the early days One does not expect any very complete historical account in a book of this kind but a reference to the pioneer work of Chester and Rice on microwave radar would have added to the value of this section

The book was written especially for the reader who is interested mainly in the fundamentals and either not particularly interested in detailed circuit techniques or already well acquainted with these Typical subjects dealt with in detail are propagation, aerials, scanning, noise, interference echoes and a valuable chapter on radar navigation systems There is a five page chapter on typical radar equipment, the reviewer feels that this is too condensed in relation to the other subjects dealt with There is a short paragraph on probable future developments It may be felt that this is very inadequately dealt with but it is undoubtedly a subject which the careful author will approach with some caution

On the whole the monograph is a satisfactory account of a very interesting subject It is a live and stimulating book as indeed one might expect when the authors are dealing with a subject to which they themselves have contributed greatly

J Sayers

Physical Aspects of Colour, *English edition*

P J BOUMA

(*312 pp, 113 illus, 9 in by 6 in*)

Eindhoven Philips Technical Library, 1949
New York Elsevier Publishing Co Inc, 1949
London Cleaver-Hume Press Ltd, 1949 30*s*

A system for measuring colour was introduced in 1931 by the International Commission on Illumination, in terms of the additive mixture of defined red, green and blue stimuli required to match any colour under test Increasing use has been made of the system in industry, but its full potentialities have not yet been generally recognized More publicity is required and in this book we have a sound objective study of the physics of colour in general and of the international trichromatic system in particular

The book was written under tragic circumstances by an expert on the subject and Dr Bouma's friends have produced a worthy memorial to him in this English translation of the original Dutch text No attempt has been made to enter the controversial field of colour vision theory but, starting from experimental data on colour matching, the representation of colours on a three coordinate system is developed and the calculation of the colour coordinates from a knowledge of the spectral composition of the light is described Once we have an unambiguous method of specifying a colour, it becomes possible to study scientifically a whole variety of problems *e g* colour tolerances, the colour rendering properties of illuminants, the spectral characteristics of dyes required to give maximum light reflection for a given saturation of colour, the principles of colour reproduction and so on

The algebra involved in these colour calculations is intrinsically easy, but in practice decidedly confusing Dr Bouma has introduced certain novel features in expressing his colour equations which seem to meet the criticisms that have sometimes been levelled at the colour algebra as written in this country, and his symbolism may well become generally adopted On the other hand, he has given a rather subtle twist to the terms brightness, apparent brightness and subjective brightness which may cause some confusion This is, however, a book that should find its way on to the shelves of all those who have any technical concern with colour

W D WRIGHT

An Outline of Statistical Methods for Use in the Textile Industry

A BREARLEY and D R COX

(74 pp, 11 illus, 28 tables, 9¾ in by 6¼ in)
Leeds Wool Industries Research Association, 1949
7s 6d net

Wool Research 1918–1948 Vol 4 Carding, Vol 6 Drawing and Spinning

(vi+244 and viii+256 pp, 155 illus, 87 tables and 119 illus, 100 tables, 9¾ in by 7¼ in)
Leeds Wool Industries Research Association, 1949
£1 1s each

THE first publication listed above is an example of material produced by the W I R A to aid the industrialist It is a small booklet designed to equip the practical man with an understanding of statistical terms and of the simpler procedures used for analysing results No attempt is made to derive any of the formulae mathematically, but a logical development of the subject is given Frequency distributions, sampling distributions, *F*- and *t*-tests and the analysis of variance are all covered, and there is a useful section on quality control The book is so short that the treatment is necessarily very compressed, and such important topics as regression analysis and the χ^2 test have been completely omitted, references are, however, given to standard textbooks for additional reading Illustrative numerical examples from textile testing, a glossary, and some useful tables complete the booklet, which should serve as a convenient summary for the industrialist or mill manager

The other two books form part of a series which the association is to produce, collecting and summarizing the research done since its foundation in 1918 It is explained that the order of publication has been determined by the needs of the industry and by the material available, so that these books, though numbered volumes 4 and 6 respectively, have been the first to appear Each deals with applied research on a single main textile process

An historical introduction in each book tells the fascinating story of the development of modern mill machinery from the primitive hand card and distaff and spindle The research which is then described is aimed at assessing the factors affecting the performance of the process A complete assessment is not yet possible but a great deal of very useful material has been collected The most important section in the carding volume is an account of an extensive series of trials on the causes of variability in woollen carding, with a detailed analysis of the results There are also several shorter reports, including some analysis based on theory and observation, of the nature of the carding action In the other volume details are given of practical investigations into the effects of changes in the design of the drawing set, or in the roller setting, twists, doublings, and drafts on a drawing or spinning frame, the overall effects of oiling and of relative humidity are also considered In both books details are given of all experimental techniques used, and the experimental results are fully reproduced

It cannot be said that either book adds anything significant to the present knowledge on these processes, however, the assembling of detailed results, which were previously scattered through many papers or sometimes unpublished, will be most useful to any investigator in this field Both books are notably well produced

M HANNAH

Books to Come

Infinite Matrices and Sequence Spaces R G COOKE *(c 272 pp, demy 8vo)* London Macmillan and Co Ltd 36s

Einführung in das Studium der Theoretischen Physik R BECKER *(c 200 pp, c 100 illus)* Göttingen Springer-Verlag

RESEARCH SUPPLEMENT

Some Properties of Nitrating Acids consisting of Nitric Acid and Sulphur Trioxide

P M HEERTJES, Dr Ir and L J REVALLIER, Ir

The melting point curve is given of mixtures of nitric acid and sulphur trioxide, also containing water and nitrous acid In the region investigated three different crystalline compounds can be distinguished

Of late, a great deal of attention has been paid to the properties of mixtures of sulphuric and nitric acids Although these are among the oldest products of the inorganic chemical industry, little was known until recently about the constitution of mixtures of them However, our insight into this problem has been deepened by recent investigations concerning the application of these mixtures for nitrating purposes

Knowledge of the properties of mixtures of nitric acid and sulphur trioxide is still very elementary, although from theoretical and practical considerations these mixtures are certainly not less important than the nitric-sulphuric acid system

Although extensive experimental work has been performed in the field of nitration with nitric and sulphuric acids, the applicability of nitric acid and sulphur trioxide mixture as a nitrating agent has hardly been investigated Only a few years ago a process was developed for the manufacture and application of such mixtures[1] Hence, it was desirable to extend our knowledge of the relatively unexplored region of the ternary system water–nitrogen pentoxide sulphur trioxide That is why in their study of the manufacture and applicability of mixtures of nitric acid and sulphur trioxide the authors also examined certain of the properties, as for example part of the melting point curve, of this system Some of the results are published in this preliminary paper

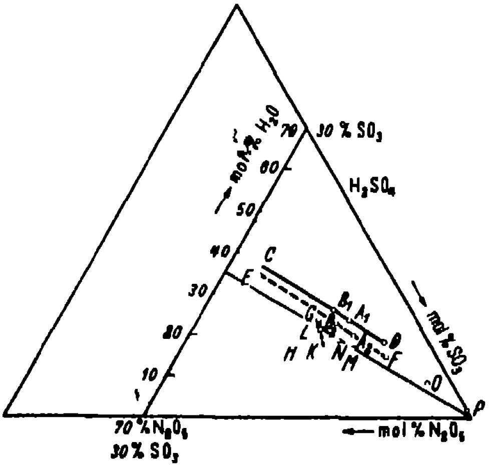

Figure 1 Part of the diagram $H_2O—N_2O_5—SO_3$

It was found that the nitrating acids obtained by adding sulphur trioxide to concentrated nitric acid (conc 99 per cent), are liquid at room temperature if the mixture does not contain more than 45 per cent by weight of sulphur trioxide

At higher sulphur trioxide contents the melting point rises rapidly and is above 100° C for mixtures containing 65 to 70 per cent sulphur trioxide If the sulphur trioxide content is increased above about 80 per cent, the nitric acid–sulphur trioxide mixture is liquid again at room temperature When preparing these nitrating acids, the formation of a slight amount of N_2O_3 (or HNO_2) cannot be avoided

Several samples were prepared by adding known amounts of acids containing about 45 per cent of sulphur trioxide, to known quantities with a sulphur trioxide content of about 80 per cent The points *C*, *D*, *E* and *F* in the diagram *Figure 1*, given in mol per cent, represent such starting mixtures which lie on either side of the crystalline region examined The melting point curves were determined by melting 1 to 2 gm of the prepared samples in a disk-shaped cuvette (*Figure 2*) The cuvettes were rotated along the axis *BC* in a paraffin oil bath

The temperature of the oil bath was raised slowly The cuvette was irradiated with a beam of polarized light, the melting

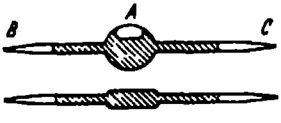

Figure 2 Cuvette used for determining melting point

Table I

Nitrating acids	*Per cent by weight*				*Mol per cent*			
	SO_3	HNO_3	H_2O	N_2O_3	SO_3	N_2O_5	H_2O	N_2O_3
C	45.7	50.9	3.0	0.4	36.9	26.0	36.8	0.9
D	81.2	16.3	2.3	0.2	72.3	9.2	18.3	0.2
E	44.7	51.9	1.9	1.5	37.1	27.9	34.3	1.3
F	80.4	17.9	1.1	0.6	74.0	10.4	15.1	0.5

Table II

Nitrating acids	*Per cent by weight*				*Mol per cent*			
	SO_3	HNO_3	H_2O	N_2O_3	SO_3	N_2O_5	H_2O	N_2O_3
Original acid G	61.8	36.2	0.7	1.4	55.1	20.5	23.2	1.2
Crystals H	62.2	36.8	—	1.0	56.6	21.2	21.3	0.9
Crystals A	63.4	37.8	−1.6	0.4	60.5	22.9	16.2	0.4
$5SO_3 \cdot 4HNO_3$ *L*	61.35	38.65	—	—	58.56	41.41		—

process being observed through a microscope The temperature at which the last crystal in the dark field disappeared was determined The air bubble in *A* ensured that the crystals were thoroughly mixed with the mother liquor

In *Figure 3* the melting point curve is given as a function of the sulphur trioxide content in mol per cent Curve *1* holds for mixtures of the acids *C* and *D* whereas curve *2* has been obtained by mixing the acids *E* and *F* The compositions of the original acids *C*, *D*, *E* and *F* are given in *Table I* The compositions of representative samples were determined by analysis and the results proved to be in fair agreement with the values calculated from the amounts of *C* and *D* or *E* and *F* that had been mixed The location of these points in *Figure 1* could only be given by neglecting the nitrous anhydride content

From the melting point curves the following conclusions could be drawn

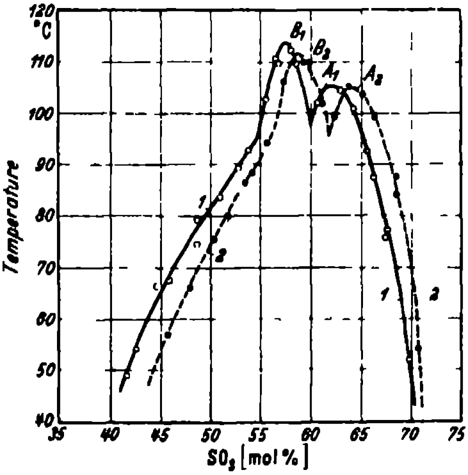

Figure 3 Melting point curve of mixtures of sulphur trioxide and nitric acid (5 to 10 mol per cent water present)

1 Two maxima can be distinguished

2 The maximum with the highest sulphur trioxide content (A_1 or A_2) can be considered to be the compound $HNO_3 \; 2 SO_3$ (point *M* in *Figure 1*) which has already been described by **COSTER** and **O CALLAGHAN**[1], **GOLFMAN**[2], and **AMELIN** and **BORODASTOVA**[4]

The crystals occur in the form of well defined rhombs By recrystallizing a mixture having a composition approximately equivalent to that at A_2, we succeeded in separating the compound *M* in a pure form The crystals of A_1, A_2 and *M* were identical in shape These crystals are represented in *Figure 4*

By means of Raman spectra it could be proved that all the nitrogen in the $2 SO_3 \; HNO_3$ compound occurred in the form NO_2^+ and that probably[6] all the sulphur was present as $HS_2O_7^-$

3 The other maximum (B_1 or B_2) may be of the compound $5 SO_3 \; 3 HNO_3$ (point *N* in *Figure 1*) This has to be confirmed, however, by recrystallization tests The crystals are fine prismatic needles, shown in *Figure 5*

The authors could not prove the existence of the compound $5 SO_3 \; 4 HNO_3$ (*L*) which has been described by **DONK**[6] It was, however, noticed that the crystals in the region 40 to 55 mol per cent sulphur trioxide differed considerably in appearance from those at *A* and *B* These crystals occurred in the form of plan-parallel plates (*Figure 6*) which appeared

Figure 4 Crystals of $2 SO_3 \; HNO_3$ (*Linear enlargement 12 2×*)

Table III

Nitrating acids	*Per cent by weight*				*Mol per cent*			
	SO_3	HNO_3	H_2O	N_2O_3	SO_3	N_2O_5	H_2O	N_2O_3
Lower layer O	90.3	8.3	0.8	0.6	86.1	5.0	8.3	0.6
Upper layer P	99.4	(0.1)	0.5	(0.1)	97.7	(0.1)	2.2	(<0.1)

The figures in parentheses are not reliable

brightly coloured between crossed nicols. Since the melting point curve does not show a maximum in this region, no information could be derived therefrom as regards the composition of these crystals. The crystals could be separated, however, from the mother liquor by draining the mixture on a porous tile. This separation is not quantitative and the analysis of the resulting solid substance was rather difficult to perform. Consequently it is not possible to give a definite conclusion about the composition.

In most samples the authors found, however, that the crystals mentioned contained less water than would correspond with the quantity present in mixtures of nitric acid and sulphur trioxide. So when a mixture belonging in the region H_2O—HNO_3—SO_3 is freed from most of the mother liquor it is possible to obtain a mixture in the region HNO_3—N_2O_5—SO_3.

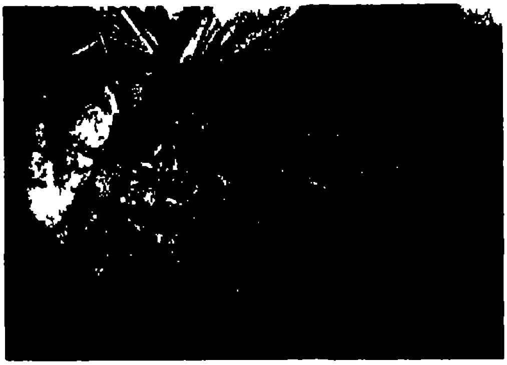

Figure 5 Crystals probably of 6 SO$_3$, 3HNO$_3$ (Linear enlargement 12.2 ×)

Figure 6 Crystals in region 40 to 55 mol per cent sulphur trioxide (Linear enlargement 23.5 ×)

This may be illustrated by the following example. From a mixture *G*, the impure crystals *H* and *K* were separated, these were obtained by draining the mixture *G* on a porous tile for 2 and 5 days respectively. The composition of these substances is shown in *Table II*, the location of the points *G*, *H* and *K* in the diagram H_2O—N_2O_5—SO_3, *Figure 1*.

The nitric acid–sulphur trioxide system described has further properties which are interesting in another respect. It was noticed that the addition of more sulphur trioxide to the liquid mixture (*e g* *D* and *F*) gave rise to the formation of a second liquid layer. This layer which consisted of almost pure sulphur trioxide appeared after the sulphur trioxide content had increased to about 90 per cent.

By way of example, the composition is given of two liquid phases *O* and *P* which are in equilibrium at a temperature of 40°C (*Table III*). At room temperature the two layers start crystallizing.

It should be remarked that the same phenomenon of two phase formation is observed with mixtures of nitric oxide and sulphur trioxide. In mixtures with a high sulphur trioxide content two layers were formed: the upper layer consisted of almost pure sulphur trioxide, the lower one containing sulphur trioxide and nitric oxide.

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A Rapid Immersion Silvering Method of High Efficiency

P B G UPTON and E F G HERINGTON, A R C S, D I C, Ph D

A method of depositing a silver film by reduction of a silver ammoniomtrate solution by hydrazine sulphate, where the deposition of silver other than on the desired surface is prevented by the presence of pyridine, is described The effect of the pyridine is shown to be due to the presence of a small proportion of surface active impurity and comparable results are found to be obtainable by the use of cyclohexylamine or ammonia instead of pyridine if a small cetyl pyridinium bromide addition to the solution is made

MOST methods of producing silver mirrors by the chemical reduction of an aqueous silver solution suffer from the defect that only a small proportion of the reduced silver is deposited as a mirror on the required surface The remainder is deposited either on the walls of the containing vessel or is precipitated in the solution and eventually forms a loose black sludge, this sludge is additionally objectionable since, besides the waste of silver involved, the precipitate may also spoil the mirror during its formation In general previous methods of increasing efficiency (*i e* the proportion of precipitated silver deposited as a mirror) have as one requirement the reduction of the rate of reaction by the addition of various interfering materials[1] In reduction by formaldehyde, SILVERMAN and HOWE[2] examined a number of possible additions and found methyl alcohol most effective, however even the optimum resultant efficiency was not much in excess of 20 per cent

In the course of some work by one of the present writers on the mechanism of the silvering process a 1 per cent solution of silver ammoniomtrate to which about 10 to 15 per cent of pyridine had been added did not show any appreciable deposition of silver on the addition of sufficient hydrazine sulphate to reduce all the silver salt present The reaction assumed was

$$N_2H_4H_2SO_4 + 4AgNO_3 + 6NH_4OH$$
$$= 4NH_4NO_3 + N_2 + 4Ag + (NH_4)_2SO_4 + 6H_2O$$

It was found that on a surface which had previously been treated with a solution of stannous chloride and washed with water, a heavy silver mirror was rapidly deposited (In the absence of pyridine of course the addition of hydrazine sulphate to the silver solution results in the formation of a silver precipitate almost immediately) *Table I* shows the rate of deposition of silver and the considerable thickness of the mirrors obtained from the solution with the pyridine addition, compared with values taken from the smoothed data of BANKS[3] for a normal type of process (using formaldehyde as the reducing agent) in which the surface was also prepared by treatment with stannous chloride

Despite this high rate of deposition maintained on the 'sensitized' (*i e* treated with stannous chloride) surface, very little silver precipitation occurred in the bulk of the solution or on the walls of the containing vessel and the solution remained perfectly clear and still usable some twenty four hours after preparation, during which time a number of separate silverings of sensitized surfaces had been made

The effect of the stannous chloride treatment in increasing the initial rate of mirror formation has been previously noted and has been shown quantitatively both by BANKS[3] and by MIYAGI and INAGAKI[4], on this basis, and in view of other work on this point by Banks and others which will shortly be published, this aspect of the present observations is at least partially understandable It was believed at first that the effect of the pyridine addition was simply to reduce the silver ion concentration to a point where the reduction for any practical purposes would not proceed in the absence of a catalyst, however, experiments with other amines which would give even lower silver ion concentration from dissociation of the general complex AgB_2OH, failed to reproduce the differential inhibiting effect of pyridine, and it was therefore concluded that either an impurity was present in the pyridine used (redistilled laboratory reagent grade) or that pyridine behaved uniquely in some way not understood Tests were made with other materials known to occur in pyridine but whilst comparable results were obtained with α and β picoline, results did not show that the phenomenon was traceable to any particular constituent

When however the process was recommended as a practical means of heavily silvering plastics in the manufacture of a special electrical component, it was found that the results obtained were markedly dependent on the source and quality of the pyridine

Table I Rate of Deposition of Silver

a 70 ml 1 per cent ammoniacal silver nitrate, *10 ml pyridine* *16 ml 1 25 per cent hydrazine sulphate*				*b Equal volumes* *6 per cent ammoniacal silver nitrate* *1 per cent formaldehyde*			
Time sec	*Silver deposited gm/dm^2*	*Time sec*	*Silver deposited gm/dm^2*	*Time sec*	*Silver deposited gm/dm^2*	*Time sec*	*Silver deposited gm/dm^2*
30	0 0064	420	0 0424	30	0 012	420	0 033
60	0 0095	660	0 0598	60	0 015	660	0 043
180	0 0216	3,600	0 164	180	0 018		
300	0 0301			300	0 028		

used and that no differential inhibition of silver reduction occurred when a sample of pyridine of purity greater than 99 9 mol per cent as established by the freezing point was used Examination of a sample of pyridine found to give satisfactory results revealed the presence of a very small amount of a surface active agent, when a sufficient amount of a surface active agent was added to pure pyridine differential inhibition of silver reduction was obtained It was also established that the variable behaviour of different pyridine samples was attributable to the varying proportion of surface active agent present The desired results could be reproduced by adding a suitable proportion of *Fixanol C* (cetyl pyridinium bromide) to 'inactive' pyridine, and the process thus becomes completely controllable The addition of increasing proportions of surface active agent to a sample of pyridine giving no differential inhibition produces results in the following sequence

1 no apparent inhibition of silver precipitation

2 inhibition of precipitation in bulk of solution but mirror deposition on walls of vessel as well as a sensitized stannous chloride treated surface

3 inhibition of precipitation in solution, no deposition on walls of vessel but good deposition on sensitized surface

4 as *3* but poor deposition on sensitized surface

5 complete inhibition *i e* no deposition of silver at all

These effects change with the age of the solution and in general any inhibited solution will start to deposit silver after some hours

These observations suggest that pyridine itself has no unique property in this process, good differential inhibitions have been obtained by adding bases instead of pyridine (notably ammonia and *cyclo*hexylamine), in suitable concentration, together with the appropriate addition of cetyl pyridinium bromide (using solutions of the order of 0 001 per cent) The following is a recipe based on the use of pyridine

The surface to be silvered is pre-treated by being wetted with a solution of 10 gm stannous chloride in 20 ml hydrochloric acid (A R) and 80 ml water The surface is then rinsed with a 5 per cent silver nitrate solution and well washed with distilled water and kept under water until required

Silvering solutions

Solution 1

10 ml of pyridine
0–50 ml of *Fixanol C* solution (0 005 per cent)
16 ml of 1 25 per cent hydrazine sulphate solution

Solution 2

70 cc of 1 per cent solution of ammoniacal silver nitrate prepared by adding 0 880 ammonia to 1 per cent silver nitrate solution until the precipitate just redissolves

Solutions *1* and *2* are mixed just before use The amount of *Fixanol C* solution is adjusted to give satisfactory results No exact quantity can be recommended as the amount required depends on the concentration of surface active agent already present in each batch of pyridine and this may change with time

The method should be of considerable use wherever the rapid and efficient deposition of a heavy silver film is required

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D S I R Chemical Research Laboratory
Teddington

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Research Correspondence

Initial Increase in Viscosity during Action of Bacterial Amylase on Starch

IN connection with an investigation on the bacterial amylase from *Bacillus subtilis* (N C T C, 2027 N)[1, 2], the author had to adapt the usual viscosimetric method for measuring amylase activity The reaction mixture used for these studies consisted usually of 15 0 ml of 2 per cent starch solution (B D H Product, vitamin and fat free) buffered to *p*H7 0 (Sorensen's phosphate buffer) and 1 0 ml of the enzyme sample While taking measurements at short intervals, it was observed that the viscosity of the reaction mixture tended to increase in the initial stages and then gradually decreased The reaction velocity curves when plotted (*Figure 1*) clearly indicate a characteristic

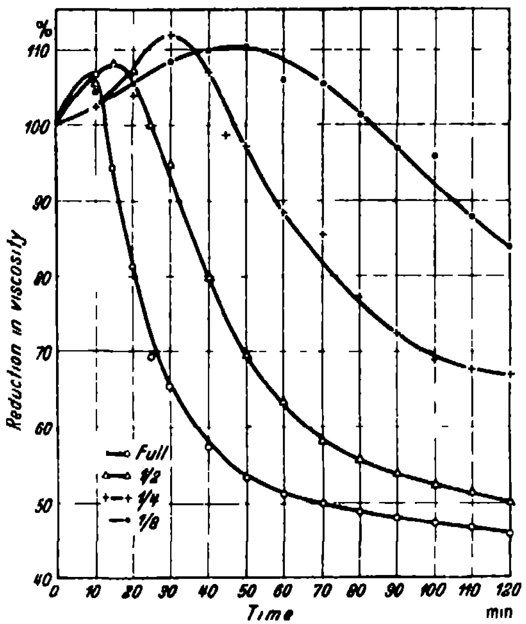

Figure 1 Time course curve with varying concentration of enzyme extract

hump in the initial stages and this becomes more prominent when the concentration of the enzyme solution is low Neither dialysis nor fractional precipitations with ammonium sulphate, alcohol and acetone of the enzyme preparation has any effect on the initial increase in viscosity Similar studies have also been conducted with other sources of amylase (ptyalin, *Amylum oryzae* and pancreas) in order to determine whether the phenomenon is a general one or only specific to certain groups The results have shown, however, that the phenomenon could be only visualized with bacterial amylase as no such characteristic hump was observed in the enzyme course of reaction curves obtained with other sources of amylase This led to the study of the chemical nature of the bacterial amylase and hence for this purpose a crude enzyme extract was subjected to systematic purification involving the following steps

1 dialysis, *2* adsorption on fuller's earth and eluting with sodium oxalate, *3* precipitation with 70 per cent alcohol, *4* precipitation with ammonium sulphate at 0 7 saturation, *5* precipitation with ammonium sulphate at 0 8 saturation, and *6* dialysis of the enzyme solution

According to the above procedure, the activity of the purified sample increased by 171 times on the basis of total solids and 48 times on the basis of total nitrogen content as compared with the original crude enzyme preparation[3] The reaction velocity curves obtained with this highly purified enzyme preparation as discussed above showed the same characteristic hump at low enzyme concentration Exactly what contributes to this hump formation is difficult to explain at this stage, but it is quite certain that the responsible factor is thermolabile in nature as the viscosity of the reaction mixture using heat inactivated bacterial amylase remains the same The observations have also been made that the bacterial amylase inhibitors such as maleic acid, iodoacetic acid *etc* are also inhibitors of this unknown factor

In the author's previous communications it has been shown that during the synthesis of amylase by *B subtilis*, vitamins of B-complex[4] and antibiotic substances[5] are formed and hence their influence on the enzymatic activity was studied The reported inhibition of thiamin on wheat amylase by PAO-CHUNG LU[6] further supported the claim in conducting the above experiments The results indicate that thiamin has no effect on the amylase activity whereas penicillin and streptomycin exert accelerating effects at high concentrations The effect of other members of the vitamin B-complex was not studied Even with the help of the above experimental data it was not possible to advance any explanation for the initial increase in viscosity, however, it is quite probable that the present phenomenon may be attributed to the formation of enzyme-substrate complex in the earlier stages of the enzyme reaction before the actual enzyme reaction (*i e* decrease in viscosity) takes place

My sincere thanks are due to Professor V Subrahmanyan and Colonel S S Bhatnagar for their keen interest in these investigations

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Valence States of Carbon and the Heats of Dissociation of CO, CN *and* N_2

EVIDENCE regarding the dissociation energies of CO, CN and N_2 has been re-examined recently by LONG[1] Independently, PAULING and SHEEHAN[2] have attempted to decide upon the correct values by the use of an extrapolation procedure Both approaches agree in indicating that the high value 11 11 ev for *D*(CO) is not correct Although the ultimate conclusions regarding $D(\mathrm{CO})$ seem to differ somewhat the attempt will be made here to show by a logical application of the principles involved that this is only apparent

The reasonable underlying assumption of Pauling and Sheehan is that linear extrapolations of the lower vibrational levels of diatomic molecules provide approximate energies of dissociation into atoms in their appropriate valence states From the estimates thus derived for the $X\,^1\Sigma$, $a\,^3\Pi$, $a'\,^3\Sigma$ and $A\,^1\Pi$ states of CO, the values obtained for $D(\mathrm{CO})$ after deduction of the valence state energies for divalent carbon and oxygen are respectively 8 76, 9 86, 9 40 and 9 63 ev This suggested that the true value is either 9 14 or 9 61 to 9 85 ev, the last being selected from a consideration of CN However a distinction between the valence energies of divalent and tetravalent carbon, coupled with an improved value for the heat of formation of CN[1], leads to the other choice

The approach of Pauling and Sheehan arbitrarily assumes that the carbon in CO and CN is everywhere divalent as in CH and $\mathrm{C_2}$, from which the value of 1 73 ev is obtained for the energy level of the divalent carbon atom This is undoubtedly true for the $X\,^1\Sigma$ ground state of CO, which contains no unpaired electrons However, the molecular properties of the $X\,^2\Sigma$ ground state of CN suggest a triple bond and tetravalent carbon (as in N≡C—C≡N, for example) This is in harmony with its chemical properties, which indicate that the free valency is on the carbon Since the change from divalence to tetravalence involves the promotion of an *s* electron on the carbon atom, the process will absorb energy Accordingly the figure to be employed here for the valence energy is not that for divalent carbon but that for tetravalent, namely 65 kcal or 2 82 ev[3] Deducting 2 82 ev plus 1 84 ev (the valence energy of nitrogen[2]) from the figure provided by the extrapolation procedure for CN ($X\,^2\Sigma$), namely 9 85 ev[2], yields 5 19 ev for $D(\mathrm{CN})$, which agrees closely with one of the possible spectroscopic values, 117 9 kcal or 5 11 ev, considered elsewhere[1] Looked at the reverse way the spectroscopic value for $D(\mathrm{CN})$ provides the estimate 2 90 ev for the valence energy of tetravalent carbon

Combining the foregoing value for $D(\mathrm{CN})$ with the entirely experimental relationship[1]

$$D(\mathrm{CO}) \quad D(\mathrm{CN}) - \tfrac{1}{2}D(\mathrm{N_2}) + 178\ 3\ \mathrm{kcal}\ (7\ 73\ \mathrm{ev})$$

it is seen that $D(\mathrm{N_2}) = 7\ 38$ ev and $D(\mathrm{CO}) = 9\ 14$ ev satisfy the equation remarkably well The alternative value 9 76 ev for $D(\mathrm{N_2})$ demands too low a value (~ 8 ev) for $D(\mathrm{CO})$, which confirms the contention of Pauling and Sheehan that it may be excluded

The latter authors derive the energy required to rupture the C—C link in $\mathrm{C_2N_2}$ by adding a conjugation energy to the energy of rupture of the C—C link in diamond Since the first process leaves the carbon in the tetravalent state, the comparison is only valid if the same stipulation is made regarding the latter, the energy of which consequently amounts to one half the heat of sublimation of diamond to carbon atoms in the tetravalent state In deriving their equations, however, Pauling and Sheehan tacitly identify this with the heat of sublimation to ground state atoms, which appears in a thermochemical equation involving $D(\mathrm{CO})$ This, apart from other uncertainties, introduces a large error into the values which follow for $D(\mathrm{NC{-}CN})$ and $D(\mathrm{CO})$ That for the latter (9 77 ev) is seen not to satisfy the foregoing experimental relationship with either value of $D(\mathrm{N_2})$

In conclusion, it is instructive to reflect that CN should possess a low lying state containing divalent carbon and a double bond Accordingly, the first excited $A\,^2\Pi$ state, with its markedly increased bond length, provides a linear extrapolation limit at 8 90 ev, a value considerably below that for the ground state The difference is 0 95 ev which, as expected, closely agrees with the difference in valence energy of tetravalent and divalent carbon (2 82 − 1 73 -- 1 09 ev) Again, the lowest excited ($a\,^3\Pi$) state of CO with its two unpaired electrons provides a further example of tetravalent carbon and extrapolates to a limit situated above that for the ground state by an almost identical amount (12 33 - 11 23 - 1 10 ev) Barring an extraordinary coincidence this is excellent confirmation of the foregoing interpretation, which not only interrelates $D(\mathrm{CO})$, $D(\mathrm{CN})$ and $D(\mathrm{N_2})$ on a satisfactory experimental footing but also accounts for the hitherto unexplained discrepancies in the linear extrapolation limits of the ground and excited states of the CO and CN molecules respectively

Deducting now the appropriate valence energies from the extrapolation limits of the $X\,^1\Sigma$ and $a\,^3\Pi$ states of CO yields 8 76 and 8 77 ev respectively as estimates for $D(\mathrm{CO})$ This suggests, in conformity with the foregoing, that the spectroscopic value 9 14 ev, corresponding to 125 0 kcal for the heat of sublimation of graphite to ground state atoms, is more probably correct than any higher value

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Commentary: An Evaluation of Animal and Human Mentality

THERE IS A MARKED UNWILLINGNESS today on the part of zoologists to concede powers of reasoning, of conceptual thought, even of intelligence, to any animal but man, though grudgingly a concession is made perhaps in the case of the higher apes These, some zoologists agree, may have the glimmerings of such mental processes It is an inevitable reaction to a former prevalence of anthropomorphic writings and utterances , but in permitting this reaction full play the zoologist, aided by the attitude of the philosopher, has succeeded in establishing a wide gulf between mankind and the rest of the animal kingdom Paradoxically this has happened concurrently with the growth of a firm belief in the close kinship between the two So we have the unquestioned and almost slavish devotion to the idea of man being the only reasoning animal

It may be unpopular, but it is the purpose here to suggest not only that we should look for and expect to find in animals mental processes comparable to those possessed by man decreasing in intensity and specialization as we descend the scale of anatomical specialization—and that human behaviour is less actuated by reason than we commonly suppose , but that the mental processes of animals, and especially of the higher vertebrates, have more of reason, intelligence and conceptual thought in them than we are usually prepared to allow

The first obstacle to an analysis of this problem is basically historical Before biology, whether human or animal, had established itself as a science, the philosophers had commenced their investigations of the mind , the words reason, intuition, intelligence and the like were being employed to describe observed mental phenomena In course of time, if not at first, it happened here, as happens in all cases of special study, that the investigators subdivided the field for convenience' sake and later lost sight of the fact that such subdivision is no more than an artificial aid Instead of treating these things as individuations of a single process, reason, intuition, intelligence and the rest appeared as single entities related to but independent of each other It is the tyranny of words in another form and is epitomized in the zest with which Descartes seized on the pineal as the seat of the soul We have, in the same way, tended to divide the individual into mind and body, and only belatedly—and by a few—is there the active realization that body and mind are but individuations of a single entity

We may speak of reason, intuition, intelligence, conceptual thought, of the conscious or unconscious mind We may subdivide even farther For example, we may speak of discursive reason, intuitive reason, speculative reason, theoretical reason, pure reason, but in so far as we fail to relate these to the total processes from which they spring so far shall we get them out of perspective Unfortunately this is what is normally done, for these subdivisions are essential for special or practical application The fault lies in this, that in returning to the broad problem we forget the roots from which they sprang and forget where the branches they represent join the main stem

The growth of an individual—leaving aside the various vegetative types of reproduction—starts with a single cell, the fertilized ovum This divides into two, apparently similar cells, and these into two again, and so on There is up to this point no indication of mind and body as separate entities There comes a time, however, when in the growth of the embryo there is a differentiation—an individuation— of endoderm and ectoderm, with later a third layer, the mesoderm (in all but the lowest animals) The finer points of the structure, function and behaviour of these layers of cells can be ignored here Two things only need be emphasized that all cells, ectodermal, mesodermal or endodermal, have a common origin, similar structure and are interdependent, and that all sensory organs are ectodermal in origin

To amplify the first of these two points, we may say that in simple terms the ectodermal layer supplies the outer covering of the body, the brain, the nerves and the sense-organs , the mesodermal layer provides the frame or scaffolding, the muscles, bones and mesenteries, heart, blood-vessels and lungs , the endodermal layer is concerned with keeping the rest alive and supplies the alimentary tract and other associated structures It might be possible at this early stage to differentiate between mind (= ectoderm = all nervous and sensory structures) and body (= endoderm + mesoderm) Even this would be an oversimplification, but less so than at a later stage , for when the body is fully formed such a division would leave us with the mind including the skin, hair, nails and sweat-glands, as well as the brain, all the nerves and all sense perceptors such as ears, eyes, nose, tongue even to the touch-perceptors over the whole surface This argument flavours of the *reductio ad absurdum* and is intended merely to emphasize that from start to finish body and mind are one in origin, function and purpose

The importance of this point is that whatever happens to the body (or soma *sensu stricto*) must inevitably affect all processes of thought The food we eat, the air we breathe, the way we carry and use the soma, all have their repercussions on the working of the brain What is more, from all we know of the fine structure of the cells, together with the gross anatomy of the organs they comprise, there is no reason to suppose that the minds of animals are different in origin, structure or function, or in the extent to which they are influenced by the soma, from those of human beings Moreover, it seems from the comparatively small result produced by a mass of so far little coordinated observational and experimental work on the behaviour of animals that we may logically assume that the difference is quantitative only Indeed, from a biologically historical point of view, if we claim to find an easy transition from the Protozoa to man (*i e* an evolution) in matters of anatomy, morphology and histology, then it is surely the simplest unassailable logic that there should be as complete a transition or evolution in matters psychological For example, we may claim that the pigment spot in a *Euglena* is the forerunner of the highly complex human eye, and that there is an easy, if not unbroken, sequence in the evolution of the vertebrate eye from the primitive ocellus by the addition of a lens, the proliferation of pigmented cells to form a retina, the addition of a diaphragm and the connection of the whole to an optic nerve We may take each organ and tissue in turn and show a similar sequence and, therefore, presumably a similar evolution We may even show the same sequence in the evolution of the brain As a matter of course we should expect the manifestations of the activity of the brain, its behaviour or mental processes as we normally call them, to show a similar evolution The human kidney is in function and structure similar to the excretory organs of a planarian worm It is more specialized and more complex but no one would deny that it is excretory And between the two, as we pass up the animal kingdom, can be found a whole series of intergradations The same thing holds true for any other primary organ , so why not for the brain ?

Either we must accept this thesis and admit that the manifestations of mental abilities found in the human being can be traced to their source at a low point in the animal scale or we must discard the theory of organic evolution as a working hypothesis It may be—and, indeed, it is highly probable—that a modification of our present scheme of evolution will be necessary Nevertheless, short of accepting some form of fundamentalism, to deny entirely conceptual thought, intelligence, reason or any other of the higher forms of mental activity in animals other than man (with possibly the higher apes) is to invite a drastic revision of biological thought In other words, amoeba can be credited with a nascent intelligence even though we have so far failed to demonstrate it , and we must at the very least reserve judgement on —certainly not deride—those who live consistently close to higher animals and claim for them mental powers which the laboratory zoologist is at present unable to admit

It is possible there is a second vector influencing the attitude of mind which is being criticized here Not only is there the tendency to underrate the mental potentialities of the brute kingdom, there is an even greater tendency to overstate the mental performances of the human We are given to understand that our human ancestors can be dated back a million years, yet if we date the dawn of civilization at 10,000 years ago we are giving a liberal estimate Admitting that the cranial capacities of the, at present, hypothetical ancestors of a million years ago were less than that of their present-day descendants, we may perhaps presume that their mental abilities were greater than those of any known anthropoid ape We are told often enough that the differences which serve to segregate man from the brute so markedly are the ability to reason, the power of speech and the opposable thumb In this statement it is clear that the ability to reason is given pride of place—as well as being treated as some peculiar and special property of the human brain Yet, in spite of these three remarkable attributes, it has taken the human race a million minus ten thousand years to climb painfully from the brute state to the dawn of civilization Moreover, in these short ten thousand years (probably much less) he has achieved the full blossoming of the civilization we know today Which, then, of the three peculiar abilities is primarily responsible for this final and tremendous spurt ? The question is significant

It is difficult to believe that the human ability to reason has increased sufficiently in this time to account for this last spurt Cranial capacities, even if we had sufficient data, could be misleading The shrew with a brain the size of a pea has as great—though not as long—a capacity for living as an elephant with a brain the size of a football We could, guardedly, say it is no less ' intelligent ' As it is, however, even the known cranial capacities of early man hardly constitute a few random samples taken at long intervals On top of this there is the considerable empirical evidence that man shows no greater exercise of reason today than he did a thousand, two thousand or three thousand years ago On the contrary, there is evidence that his unsolved problems of living are increasing in number at an accelerating rate Presumably all hominoids had an opposable thumb, so that we are left with the third and last peculiar ability, the power of speech, to explain man's dominance The available evidence suggests that this is of comparatively recent development

Man's achievements in the last few thousand years do not lie in the field of wisdom In fact, one is tempted to suppose that here there has been, in this particular, retrogression In cleverness we have forged ahead, but this is almost entirely a technological achievement, the result of being able to grasp and use tools and, what is much more important, build up a cultural inheritance of books, buildings and implements of all kinds to enable succeeding generations to profit by the achievements of those that have gone before Chronologically we might expect that the use of articulate speech, and particularly of writing, antedates by very little the dawn of civilization and is primarily responsible for the rapid growth of so-called human progress Using, again, the *reductio ad absurdum*, let us try to visualize a community of human babies planted at the moment of birth in the middle of a prairie where they could not at any time catch a glimpse of civilization or of civilized human beings If—assuming they could survive until the normal weaning period—such a thing were possible, they would start the long million-year climb and their descendants would probably arrive at the end of the time with a civilization much as we now have In the meantime, however, would an invisible observer see in them any markedly greater mental abilities than in, say, a similar swarm of chimpanzees ? In other words, the achievements of civilized man are due not so much to inherent abilities as to being surrounded by an inherited artificial environment, with the advantages of a cultural heritage, which must of course include the system of education

It does seem that we look around at the tremendous achievements of civilized man , we take note of our own individual achievements, based on the advantages of a cultural heritage , and we see with pride the earth, sea and sky subjugated to our whims At that moment we deceive ourselves into accepting these things as individual achievement Even the most humble of us probably do no more than credit the present generation, maybe with the help of the two previous generations or so, with the achievement It must be seldom that a *homo sapiens* recalls that it is the product of a million years and of millions of individuals In fact, if a man stops to reason he realizes that reason has had little to do with it , and that, ironically enough, man has individually comparatively little ability to reason The achievements of the human race are the accumulation over many years of many individuals having mental capacities slightly greater than those of the best-blessed animals What each individual does possess, however, is the advantage—and this is what marks him most of all from the brute—of being able to express himself in the spoken word by imitating his parents and in the written word by receiving suitable guidance from specially trained mentors

It is usual to postulate that man is a conscious animal, conscious of himself, and that this is another peculiar feature setting him apart from the mere brute Certainly he is conscious of his achievements but that does not make the actions or motives leading to the achievement conscious actions or motives We know that a cock blackbird sings well in spring because his reproductive glands are in full condition , but we have no means of deciding whether or no he is conscious of the achievement represented by that song Some of us suspect he may be conscious of it, and proud of it Again, the determining factor in the hen blackbird's building of a nest is endocrinal This does not, however, exclude the possibility that she is consciously proud of her work Those who live close to animals are inclined to believe in this conscious pride, in their offspring or in other miscellaneous and lesser achievements A cock blackbird will flee a prowling cat outside the breeding season, but let that same cat menace his fledgeling brood and he will 'dive-bomb' the cat with lion-hearted courage The actuating motive is clearly endocrinal , but there is surely a consciousness of danger, a consciousness of parental responsibility and other things beside In any case, as postulated earlier in this article, all mental effort is based on a physical plexus of events , and all animal behaviour is the result of a psychophysical interdependence, whether conscious or unconscious And the same is true for man In other words, human behaviour is like that of all animals fundamentally intuitive and consciously rational to a very minor degree only

A slight digression may be profitable at this juncture to amplify one point the use of the word 'intuitive' The human brain at the moment of birth is void except for the inherited reflexes and possibly some 'racial memories' From the moment of birth the sole contact with the world is through the senses and there can be little doubt that the wealth of minutely detailed impressions passed through them to the brain is immense This wealth of sights and sounds, tastes and smells, and tactile impressions of both minor and major importance, and of infinitely varied type and quality, fill in the background of what we call experience Their re-sorting and re-grouping, their amalgamation and synthesis by the brain cells is continuous and involuntary Their influence on our thoughts, conscious and unconscious, is none the less tremendous because normally unheeded These are the intuitive—the non-consciously learned—experiences, and the intuitive behaviour they produce forms more of our daily routine than does that arising from deliberate learning They are responsible for more of our conditioned reflexes than we suspect Moreover, these same inherited reflexes, possibly racial memories, and intuitive behaviour differ little in quantity and quality as between human and animal except in so far as anatomical specializations differ In other words, deprive the human race of learning derived from books, the use of tools and all other components of our cultural heritage and the margin between the human and the best brute is a small one.

Occasionally there comes to light a case in which a child has been kept in a bare room for years, without toys or books, without contact with normal society. In all such cases the children are near-animals, in the more extreme cases they have hardly the power of articulate speech. Such cases throw into bold relief how much we depend for our vaunted mental superiority on our ability to make use of records, whether in books, metal or stone, handed on from generation to generation.

The purpose here, as already stated, is to suggest that we err in denying in other animals mental potentialities similar to our own, though they be quantitatively inferior. Human behaviour is determined by the same plexus of inherited, unconditioned reflexes, to which are added the conditioned reflexes derived from experience (which includes a protracted period of education), and these in turn are influenced by seasonal and diurnal metabolic changes and rhythms. It appears more purposive and rational to us because it is related to an environment which we understand, and it is well to recall that domesticated pets or wild animals hand-fed from birth and fixated on human beings appear to us more intelligent than their wild brothers for the same reason. If, however, we can discount the appearance of purpose and rationality derived from this environment—this cultural inheritance—then the manifestation of human mentality, viewed objectively, would show comparatively little more of reason, intelligence or conceptual thought than many species of mammals or birds.

If we are to evaluate successfully the absolute mental potentialities of animals it will be necessary not only to observe and document more closely their actual behaviour but to relate it to their environment. And in comparing it with our only yardstick, our own experience of human mental potentialities, we must make due allowance for man's tremendous advantages in the expression of thought. The grasping thumb and the power of articulate speech are tools only, linked with mental processes but not an integral part of them. It would seem that too often in our assessment of human mental abilities we are prone to judge the power of the dynamo by the efficiency of the tools it drives.

A last word may, perhaps, be permitted on the need for caution in our observation of animal behaviour. Under simple conditions it is possible for a human being to live quite well for the major part of his time without active thought. That is, *unconditioned and conditioned* reflexes are sufficient for normal living, the higher mental activities *i.e.* thought, being called into play mainly in moments of stress or crisis. Given that animals are not pure automata, we should expect the same to be exactly true for them. For the greater part of the time, therefore, we should expect their observed behaviour to be a manifestation of these reflexes. Behaviour manifesting anything more than this must necessarily be rare, and its observation the result of the lucky accident. Perhaps much of our scepticism arises from an increasing unwillingness to accept those things that cannot be tested in a laboratory. But in a laboratory we cannot test 'crisis-behaviour' of a wholly unnatural kind. [It may be accepted that only the more successful human beings, and more especially those living under civilized conditions, are subject to an abnormally high incidence of such 'crisis-behaviour'.]

It may be that, in what has been said here, the case for the non-human animals has been over-stated and that for the humans under-stated in some particulars. It would be surprising if this were not so, for in this space generalizations only are possible and we are up against the initial difficulty that the human race, including fossil men, comprises a handful of closely similar species, whereas the rest of the animal kingdom, even excluding fossil species, comprises nearly a million very diverse forms. Nevertheless, two things can be claimed. A timely warning may have been sounded against under-rating the mental capacities of animals, and against overrating those of human beings. As to the last point, the most valuable service that can be rendered to the human race in this era of breath-taking technological development is the inculcation of a little humility regarding the potentialities of the human brain.

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Measuring Fringe Orders in Photoelasticity

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CERTAIN transparent materials become doubly refracting when stressed, this double refraction can be shown and measured by placing the stressed material in a polariscope In its simplest form the plane polariscope consists of an optical bench with a single light source and two polarizing devices, for photoelastic work this instrument is usually converted into a circular polariscope, by the insertion of two quarter wave plates The amplitude of light vibrations in such apparatus is the same in all directions normal to the direction of propagation The nicol prism has been superseded as a polarizing device in photoelasticity by *Polaroid*, transparent sheet material containing specially orientated iodoquinine sulphate crystals which have the property of transforming a ray of unpolarized light into two plane polarized rays and absorbing one of these, a light wave being transmitted which is uniformly plane polarized

FORMATION OF INTERFERENCE FRINGES

A ray of polarized light entering normally a sheet of doubly refracting material subjected to stresses in its own plane is transformed on entry into two rays polarized respectively in the planes of maximum and minimum principal stress It can be shown mathematically that these principal stresses are always mutually at right angles and that there is no shear stress along the planes of principal stress It is conventional to regard a tensile stress as positive and a compressive stress as negative

The stress-optic law— The velocity of transmission of each of the rays differs from that in the unstressed material by an amount proportional to the associated principal stress Hence on leaving the sheet one ray has been retarded relative to the other by an amount proportional to the thickness of the sheet and to the algebraic difference between the principal stresses, a statement known as the stress-optic law This law is expressed by the equation

$$R = Cd(P - Q) \qquad (1)$$

where R is the relative retardation in Ångström units, d is the sheet thickness, and P and Q are respectively the maximum and minimum principal stresses C is a constant for the material and is called the stress-optical coefficient it is expressed in brewsters (10^{-13} cm^2/dyne), a unit named after Sir DAVID BREWSTER, the formulator of the stress-optic law

Fringe order— If the relative retardation amounts to one wavelength or any integral number of wavelengths the emergent rays combine to form a ray vibrating in exactly the same plane as the entering ray, in a crossed polariscope this ray will be extinguished If a completely stress-free photoelastic model is placed in a crossed polariscope *i e* with the analyser set so as to produce extinction of a direct ray, the light passing through it will be extinguished and the whole model will appear dark When load is applied to the model the stress distribution is determined by the shape of the model In general $(P - Q)$ varies from point to point this variation causes similar variations in R, since C and t are constant throughout the model With monochromatic light the fringes where R is a whole number of wavelengths appear dark being separated from each other by bright fringes The relative retardation expressed in wavelengths at the successive dark fringes is known as the fringe order Black and white fringe photographs show the fringe pattern as viewed in monochromatic light

Figure 1 shows a fine example of black and white fringe photography[1], obtained with a model made from *Glyptal, BT 61 893*, a synthetic resin prepared from polyhydric alcohol and phthalic anhydride The two elongated projections were equally loaded normally at the centre of each upper flank, as shown by the arrows The bending moments on the projections, combined with the curvature of the fillet produce stress concentrations on both sides of the roots of the projections, at the tip of each projection, which is stress-free the fringe order is zero Along the unloaded part of the boundary there is only one principal stress, P if tension is involved, Q if compression The fringe order at any point on such a boundary therefore indicates the value of this boundary stress The peak values, which are very localized, are indicated, as well as the point where the boundary stress changes from compression to tension

The higher the stress-optical coefficient the greater the fringe order for a given $(P - Q)$ and t Thus for the most convenient thickness, say ¼ in (6 4 mm), the maximum useful fringe order depends on the stress-optical coefficient and on the limit of

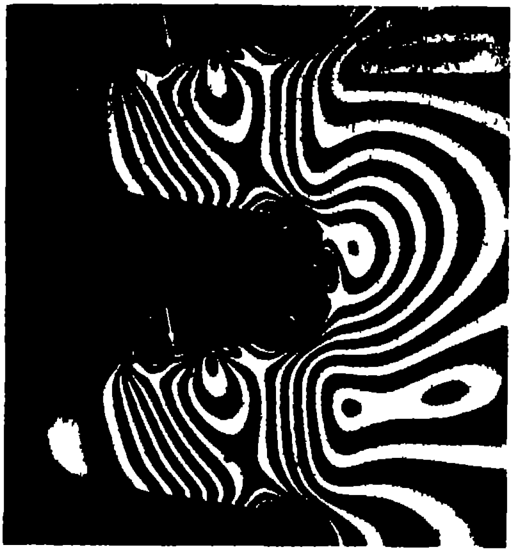

Figure 1 *Fillet stresses due to loads on projections Model fringe value 332 lb/in² (23 34 kg/cm) Thickness 0 263 in (6 68 mm) Loading 200 lb (90 72 kg) per tooth*

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proportionality of retardation to stress which may be as high as or even higher than the elastic limit

When white light is used the first order extinction can only occur for one particular wavelength at a time Thus a coloured band is seen, the colour being that complementary to the extinguished light Consequently for retardations varying from zero upwards the first visible light to be extinguished is that with the shortest wavelength *i e* the violet Similarly the last primary extinction is that of the red, leaving green Hence, starting from darkness, a definite sequence of complementary colours is obtained for the whole range of the visible spectrum With retardations greater than one wavelength in the extreme red the cycle is repeated with rather simpler colour variations Attempts have been made to measure the retardation by colour matching , but this is somewhat crude and inaccurate The purpose of this review is to discuss the various methods of measurement which are, as far as possible, independent of personal judgement

Table I shows approximate values for the stress-optical coefficients, Young's modulus, and the elastic limit of some common photoelastic materials from which it can be inferred that the highest useful fringe order varies greatly with the nature of the material, and that the choice of material decides the method of measurement

DEFINITIONS OF PHOTOELASTIC TERMS

It is necessary to explain two terms now current in photoelastic work, the material unit fringe value and the model fringe value

Material unit fringe value, F—Equation 1 gives the relative retardation R in Ångström units for a thickness d mm when C is expressed in brewsters and the principal stresses P and Q are in bars *i e* megadynes/cm² In practice, engineering units are employed for d and for $(P - Q)$ Equation 1 still applies if C is measured in appropriate units Thus

$$\underset{\text{Å}}{R} = C \times \underset{\text{cm}}{d} \times \underset{\text{kg/cm}^2}{(P - Q)}$$

where C is in units of 1/9 81 brewster, or

$$\underset{\text{Å}}{R} = C \times \underset{\text{in}}{d} \times \underset{\text{lb/in}^2}{(P - Q)}$$

where C is in units of 1/1 752 brewster

Then for unit thickness, the fringe order

$$N = \frac{R}{\lambda} = \frac{C}{\lambda}(P - Q)$$

Thus for $N = 1$

$$(P - Q) = \frac{\lambda}{C} = F \qquad (2)$$

where F is the material unit fringe value

Table I *Properties of Photoelastic Materials*

Material	*Stress-optical coefficient C*	*Young's modulus*		*Creep*	*Stress-strain proportional limit*	
		10⁵ lb/in²	*kg/cm²*		*lb/in²*	*kg/cm²*
Borosilicate glass	2 3	100	703 000	*Negligible*	8,700	610
Plexiglas *Perspex* *	4–6	5	35,150	*Negligible up to 7 000 lb (3,178 kg)*	7,000	490
Celluloid	5 4–9 6†	2 5–3 3	18,000–23,000	*Moderate*	—	—
CR 39 (allyl styrene resin)	30 35	2 8–3	19,000–21 000	*Small below 15 C*	7,000	490
Glyptal (e g BT 61–893)	38–40	6 3	44 300	*Very slight*	5,500	390
Phenol formaldehyde resin (e g Catalin rod)	62–70‡	1 9‡	13,500	*Considerable*	—	—

* Unplasticized † Increases with aging ‡ Dependent on loading time

Model fringe value— In a model of thickness d made from a material where the unit fringe value is F the principal stress difference giving a fringe order N is FN/d F/d is known as the model fringe value Thus, to convert fringe order to stress, we have

$$(P - Q) = \text{Fringe order} \times \text{model fringe value} \quad (3)$$

Although the material fringe value for a given wavelength is characteristic of the material, varying inversely as the stress-optical sensitivity, it may vary slightly from batch to batch and is dependent on temperature It is also affected by creep In practice, therefore, the model fringe value, when required, is determined by loading a simple calibration specimen cut from the same sheet The fringe order is observed at a part of this specimen where the stress is uniaxial and can be exactly calculated from the applied load At such a point if $Q = 0$ and $P = T$ (a known value), T/N is the model fringe value For materials subject to creep the time of loading must be the same in the calibration specimen as in the model

MEASUREMENT OF FRINGE ORDER

Two distinct methods of measuring fringe order are employed, measurement by fringe count, which is used with highly sensitive materials, and measurement by compensation

Measurement by fringe count— In an instance such as that shown in *Figure 1* it is sufficient, in measuring the peak boundary stress, to estimate the fringe order to the nearest half unit by inspection of the photograph, since the maximum fringe orders are quite high It is seldom possible completely to avoid time edge stress A small amount of edge stress is evident in *Figure 1* from the sudden change in direction of the fringes near the boundary However as was shown by R B HEYWOOD[6], it is possible to correct boundary fringe observations by taking a set of readings at different loads and plotting fringe order against applied load This method was employed in evaluating the fringe orders in *Figure 1*

Greater accuracy can be obtained at lower fringe orders by observations on the model itself first with dark field and then with field of maximum brightness The light and dark fringes are thus reversed *i e* with bright field the centres of the dark fringes give positions of exact half integral fringe orders It will be seen that, the model fringe value being known, estimation of $(P - Q)$ requires no special apparatus when there is a sufficiently high fringe order since the fringe orders are apparent

Measurement by compensation— It may not always be desirable to use a material with a high stress-optical coefficient, or again, it may be necessary to employ a sheet, or a slice, of material much thinner than normal The ratio of thickness to the size of geometrical features *e g* holes, is limited by the necessity for ensuring that no appreciable stress is present in a direction normal to the plane of the sheet Also, too thick a model causes a space effect at the boundaries, ½ in (*c* 1 cm) is an outside limit for plane photoelastic models Such materials as glass, celluloid, and *Plexiglas* do not permit a fringe order greater than one for glass to four for *Plexiglas* When these materials are used the fringe order must be measured with an accuracy of 1/10 to 1/20 fringe or higher This is done by compensation *i e* by introducing a measurable counter retardation just sufficient to restore darkness The net retardation is then zero Compensation with instruments is usually carried out with white light as the counter-retardation is gradually increased from zero the resultant colours retrace the succession introduced by stressing the model till finally complete extinction indicates that full compensation is attained The retardation can then be read off on the instrument

COMPENSATING INSTRUMENTS

Although compensating instruments are rarely used nowadays they will be reviewed briefly as illustrating the fundamental principle of photoelastic measurement

There are two systems of compensation by the use of instruments The first type, that used by Coker with celluloid models[8], measures stress directly, the second type produces a relative retardation by crystal-optic means

The Coker compensator— The Coker compensator[8], a somewhat expensive instrument, might well be termed a 'comparator' It consists of an adjustable frame into which a strip of material made from the same piece as the model is mounted The strip is shaped so as to produce a uniform tensile stress in the middle portion when axial tension is applied the tension is shown by a small but accurate specially designed spring balance To use the instrument the directions of principal stress at the point in question are ascertained and the compensator is placed with its axis in the direction of the minor principal stress so that the light from the point of the model under investigation traverses the middle portion of the strip Tension is then gradually applied until extinction occurs, white light being used From the load reading the stress in the strip can be immediately deduced if this single stress is T then, from the stress-optic law,

$$(P - Q) = T \quad (4)$$

It will be noted that this method is independent of temperature variations, since these affect equally the model and the strip

Babinet compensator— This form of compensator uses two adjustable quartz wedges The Babinet-Soleil compensator is a modified Babinet type which gives a uniform bright or dark field

Berek compensator— Another type of crystal compensator, the Berek, convenient for use in the polarizing microscope, produces differential retardation by the tilting of a thin crystal slice A compensator of this type with a field of several square inches can be made by using either lepidolite or *C R 39* synthetic sheet These avoid the expense of accurate grinding and polishing

TARDY METHOD OF COMPENSATION

We now come to a method of compensation which, though requiring no special instrument, can be more accurate even than the instruments already mentioned Introduced as long ago as 1929 by H L TARDY , this method seems to have been unduly neglected It uses rotation of the analyser for compensation The light used must be monochromatic and it is necessary that the quarter wave plates should be truly quarter wave for the wavelength employed With the neutral lines of the quarter wave plates set at + 45 and − 45 respectively to the plane of polarization and the analyser set for extinction, we have what is termed the crossed circular polariscope, see *Figure 2* Assume that the second quarter wave plate and the analyser are set to any arbitrary direction as shown in *Figure 3* Take as directional axis a line Ox not fixed in space, but at 45 to the neutral line of the second quarter wave plate, and let θ denote the counter-clockwise angle of rotation of the analyser from the line Ox as shown

Consider the ray which passes through the model at a point where the birefringence is characterized by the difference in phase φ and by the angle α made with Ox by one or other of the axes of principal stress, Oy and Oz, *Figure 4* It can be shown that the observed light intensity is proportional to the factor

$$K = \sin^2\left(\frac{\varphi}{2} - \theta\right) + 2\sin\theta\sin 2\theta\sin^2\alpha \tag{5}$$

Consider the conditions

1 $\theta = 0$, $\angle AOQ_2 = \angle AOx = 45°$—From equation 5 it follows that under these conditions the intensity at any point is independent of α *i e* of the direction of principal stress and of the orientation of Ox The intensity is proportional to $\sin^2(\varphi/2)$ It is this relation that produces the alternate light and dark fringes, which are independent of the direction of principal stress

Hence if the analyser and its quarter wave plate, maintained at 45° relative to each other, are rotated together, θ remains zero and there is no change in intensity This can easily be verified with a polariscope having the second quarter wave plate coupled to the analyser

2 $\theta = \theta_1 \neq 0$ It follows from equation 5 that the factor K is now zero only if one or other of the following double conditions is fulfilled

$$\frac{\varphi}{2} = \theta_1 \text{ and } \alpha = 0$$

or

$$\frac{\varphi}{2} = -\theta_1 \text{ and } \alpha = \frac{\pi}{2}$$

since if $\alpha = 0$, $K = \sin^2(\varphi/2 - \theta_1)$ and if $\alpha = \pi/2$, $K = \sin^2(\varphi/2 + \theta_1)$

Now $\alpha = 0$ or $\pi/2$ if one or other of the directions of principal stress in the model coincides with Ox With this condition, unless $\varphi = 0$ or an integral multiple of 2π, the observed light intensity will not be zero in the crossed position Hence when the analyser only is rotated from Ox through an angle $\varphi/2$ it will produce extinction

There are two possible methods of applying these properties of the polariscope, rotation of the analyser alone or rotation of both the analyser and its quarter wave plate

Rotation of the analyser alone— To show the directions of principal stress, the polariscope is temporarily converted to a plane polariscope by removing the quarter wave plates The polarizing axis is set in the direction of either principal stress by turning polarizer and crossed analyser together, until the centre of an isoclinic line is at the point in question

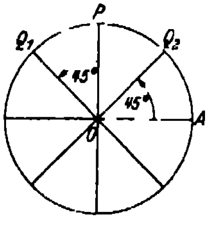

Figure 2 *Diagram of crossed circular polariscope OP, axis of polarizer OQ₁, OQ₂, axes of quarter wave plates OA, axis of analyser* $\angle Q_2OP = \angle Q_1OP = 45°$

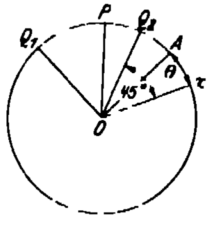

Figure 3 *Analyser and quarter wave plate disturbed,* $\angle Q_2Ox = 45$ $\angle AOx = \theta$

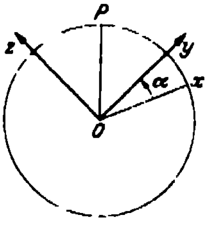

Figure 4 *Directions Oy and Oz of planes of principal stress in model*

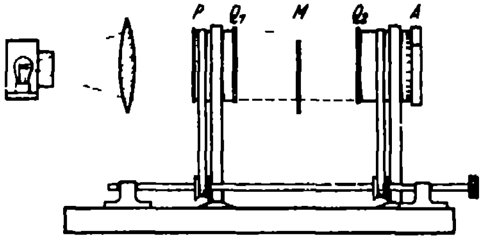

Figure 5. Arrangement of polariscope for Tardy method of compensation. P, polarizer; Q_1, Q_2 quarter wave plates; A, analyser

The quarter wave plates are then restored to $\pm 45°$ and the analyser is rotated through such an angle θ_1 as will produce complete extinction. This produces a compensation $\varphi = 2\theta_1$; by measuring θ_1 the amount by which φ exceeds, or falls short of, an integral value of 2π is known. In practice there is no difficulty in distinguishing between the additive and subtractive directions of rotation.

For convenience in using this method it is best to provide a positive coupling between analyser and polarizer, as shown in *Figure 5*. The quarter wave plates are mounted so that they also rotate, a special rotary movement of the analyser alone being provided, with a scale marked directly in decimals of a wavelength. Since $\theta_1 = 180°$ corresponds to a full wavelength, each 18° rotation of the analyser corresponds to 0.1 wavelength.

It may be mentioned here that although with perfect quarter wave plates it is unnecessary to vary the position of the polarizer and the first quarter wave plate since the light entering the model will be perfectly circularly polarized, in practice the plates can never give exactly the right retardation. Usually, however, they are both cut from the same sheet and are optically equal. In the crossed position, with equal plates, it can be shown[4] that up to ten per cent error in retardation makes no appreciable difference to extinction. When using the Tardy method greater exactness is required; the errors are minimized, however, if the plane of polarization coincides with one or other of the principal stresses.

In a model with several orders of fringes present the effect of rotating the analyser alone can be readily demonstrated. Let two neighbouring dark fringes be selected at a position where the directions of principal stress are sensibly constant; let these directions be set parallel and perpendicular respectively to the axis of the polarizer. Starting, as always, from the crossed position, a positive rotation of the analyser shifts the fringes one way and a negative rotation shifts them the opposite way. For a rotation of 90° in either direction the light and dark fringes will have changed position, *i.e.* the effect will be the same as interposing a half wave retardation plate with its axis along one or other of the principal stresses. This half wave retardation plate may be imagined to have been replaced by a Coker compensator stressed to half wave retardation. By a further rotation of the analyser through 90° each dark fringe will have shifted to the position originally occupied by its neighbour, and the original pattern will be restored. That this must be so is obvious from the fact that the analyser is now in the same alignment due to a total rotation of 180°, as it was originally. The same effect would have been obtained by increasing the stress in the imagined Coker compensator so as to produce exactly one wave retardation. Hence for any rotation θ radians of the analyser, $\theta \ngtr \pi$, the effective compensation produced is θ/π wavelength.

Rotation of both analyser and quarter wave plate. Tardy used a somewhat different procedure in plotting fractional fringe orders in optical glass, where the maximum retardation was less than one wavelength. Referring to condition 2, it was shown that with $\alpha = 0$, $K = 0$ when $\varphi/2 = \theta_1$ and that with $\alpha = \pi/2$, $K = 0$ when $\varphi/2 = -\theta_1$. Whether $\varphi = +2\theta_1$ or $-2\theta_1$ the fractional fringe order is θ_1/π. Thus viewing the whole model through the analyser set at angle θ_1 to Ox, and therefore at $\pi/4 - \theta_1$ to its quarter wave plate, extinction will occur only at the intersection of the fractional isochromatic, *i.e.* locus of constant relative retardation, θ_1/α, and the isoclinics α and $(\pi/4 - \alpha)$. By maintaining the same relative position θ_1, *i.e.* rotating analyser and quarter wave plate together, it is easy to plot the complete isochromatic. Taking a new angle θ_2 another fractional isochromatic is found in the same manner, and so on[7].

PHOTOMETRIC METHOD FOR GREATER ACCURACY

In practice, visual determination of the setting for total extinction at a selected point is rather inexact. A valuable refinement employing instrumental means has been recently made by A F C BROWN and V N HICKSON[8]. These workers have developed a sensitive photoelectric photometer which can give a precision of 1/500 wavelength retardation. In this instrument constancy of standard illumination is secured by means of a special circuit for providing constant input voltage; the only drawback to the scheme is the rather high cost of this unit. An enlarged image of the model is projected on to a movable vertical screen on which the photometer is mounted. A small hole in a metal plate placed in front of the photoelectric cell transmits the light from a very small area of the model, e g with nine to one magnification a ⅛ in (3.175 mm) diameter hole corresponds to a spot of only 0.014 in (0.356 mm) diameter on the model Thus observations can be made very close to the edge, overcoming a defect inherent in the original Tardy method Although actual boundary values cannot be measured, these can be computed with only small extrapolation The following advantages are claimed for the photometric method

- *a* no personal error is involved in determining minimum intensity
- *b* good accuracy is obtained with low sensitivity materials
- *c* non-uniformity of the field brightness or of model transparency are not important
- *d* in frozen stress work smaller loadings and reduced strains can be used, also thinner slices are possible where boundary stresses are required at an edge which is not normal to the plane of slicing
- *e* the photometer shows the central axes of isoclinic bands and is able to discriminate between the coloured isochromatics and the black isoclinics

CONCLUSION

The measurement of fringe orders, though the most important work in photoelasticity, does not of itself provide the information required for a complete analysis in the interior of the model The photoelastician must be fully acquainted with such analytical processes as the plotting of isoclinics and stress trajectories He should be familiar with Frocht's slope-equilibrium method and shear difference method of integration Filon's method of graphical integration and, above all the iterative method of harmonization for determining $(P + Q)$ These processes are fully described in books and papers mentioned in the references[3, 5, 9, 12]

Acknowledgement is made to the Chief Scientist of the Ministry of Supply for permission to publish this article

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Recent Progress in Refractories

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ENGINEERS unfamiliar with steelplant conditions would be appalled to hear that an elegant structure costing as much as £100,000 was only intended to last about a year, and would be heavily damaged within a few weeks Further, that the roof which one moment looks perfectly smooth because it is operating 20C° below its maximum safe temperature might soon be a mass of stalactites due to localized flame impact

Such critical conditions are a perpetual challenge to the refractories technologist and this, together with the fact that iron and steel works consume about half the refractories produced, explains why most of the recent improvements have been in this part of the field

SILICA

Almost all open hearth and arc furnace roofs are built of silica bricks The opinion is frequently expressed that silica is already giving as much service as can be expected from it, but such statements ignore two important points

1 the remarkable improvement in life that can come from a rise in refractoriness of only a few degrees such as might result from a reduction of 0.5 per cent in the alumina content;

2. the striking effect on durability of reduced porosity.

Numerous reports[1-4] from the United States show that super-duty silica bricks with a total alumina, alkali and titania content of less than 0.5 per cent are markedly better than the normal product containing 1 to 2 per cent of these impurities. Equally remarkable results have recently been obtained in this country using bricks combining low alumina content with abnormally low porosity.

Recent research on flow patterns in furnaces[5, 6] suggests that localized wear in roofs is probably due in the main to the impingement of hot waste gases laden with iron oxide and moving at high velocities. Satisfactory aerodynamic design should ultimately reduce wear very considerably, but the steelmaker will doubtless offset this gain by raising the operating temperature and hence the production rate.

One of the difficulties in correlating brick quality with performance has been the slowness of normal alumina determinations. It would now appear that the spectrograph[7] offers a rapid and satisfactory method and this, together with the split roof technique developed by H. M. KRAMER[8], should greatly accelerate research. In this latter method one half of the roof is built with the standard brick and the other half with the experimental brick. The weight of material used for repair in each half is noted and the life of the two halves expressed as a corrected figure representing the life which might have been expected had no patching occurred. If such corrected lives are plotted against alumina content it will be seen that a reduction in alumina content of even 0.5 per cent is worth a good deal of effort.

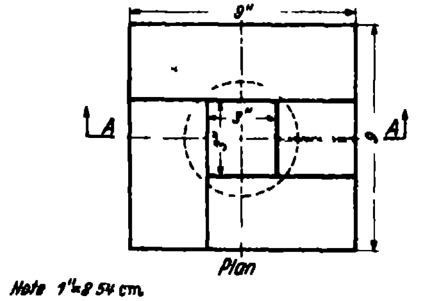

Figure 1 *Sketch of apparatus used for spall tests on silica bricks*

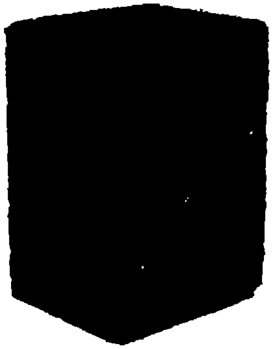

Figure 2 *Effect of thermal shock on silica test piece*

The spalling of silica bricks due to excessive initial heating rates should now be considered as pathological[10], since it can always be avoided by working to a controlled schedule of, for instance, 24 hours to 600°C[9]. Even so the work of T. W. HOWIE[11], who determined the maximum safe rate of heating for test pieces or full bricks heated from one end by means of an electrical hotplate (*Figure 1*), warrants careful study because it throws a good deal of light on spalling troubles. During each test the temperatures at the hot face and at various distances behind it are measured with thermocouples passed through holes in the surrounding insulating bricks. *Figure 2* shows a typical sample after test. It will be noticed that the cracks are always furthest from the hot face at the corners, a phenomenon observed in service where spalling usually results in a cobblestone appearance on the underside of the roof. Howie showed that the distance of the crack from the hot face decreased with the rate of heating. This agrees with works observations, a silica brick placed over a hole in a hot furnace flaking off in extremely thin layers. As the rate of heating is decreased the position of the crack moves back from the hot face and eventually it disappears. This explains why roofs heated up with some care, though not carefully enough, often start to spall several weeks after going into service. Observations of such roofs at the end of the campaign, *Figure 3*, show that they are frequently split into two halves, but that it is not until an odd half brick falls away and the key is lost that a shower of spalled fragments falls into the bath. The brick shown at the centre of the arch in *Figure 3* evidently cracked and then dropped a short distance before becoming wedged. The surface of the roof subsequently glazed over holding this evidence of early cracking securely in position.

Even where no thermal spalling has occurred a peculiar type of spalling, as illustrated in *Figure 4*, may be experienced. It has long been known that the fluxes in silica bricks tend to migrate to a zone several inches behind the working face. If now the face of one such brick comes away the low melting point zones in the adjacent bricks may be exposed and tend to soften The weight of the lower parts may then be sufficient to pull the roof into two halves and melting may occur simultaneously both at the original and at the new working face

Some of the peculiarities experienced with silica bricks, particularly in reducing atmospheres, may be explainable in terms of the work of C A ZAPFFE[12], who suggests that wear may sometimes be due to volatilization of silicon monoxide

MAGNESIA

There exists at the moment an urgent need for a refractory that will withstand large concentrations of iron oxide at a temperature of, say 1 700°C Magnesia does not melt until 2,800°C i e at least 1,000C above the melting point of a silica roof, and can absorb large quantities of ferrous oxide without serious loss of refractoriness It does not show the abnormal growth associated with chrome magnesite bricks, nor does it shrink badly as do some dolomite refractories due to the formation of low melting point calcium ferrites It has not become the universal refractory because it does not remain in position to be attacked After a few weeks of apparently perfect behaviour it begins to crack and large pieces come away from the working face This failure is frequently attributed to differential thermal expansion of the slagged and unslagged parts, but this suggestion is not borne out by laboratory tests The damage is more likely to be due to differences in modulus of rigidity or to long time creep of a refractory which at working temperatures must be rather like wet sand Many of the properties of magnesia bricks are still those of the bond, no one having yet developed a commercial magnesia brick that is intercrystallized

Figure 3 Open hearth furnace roof showing spalled brick held in position

Figure 4 Sideways attack on silica roof bricks leading to separation of working face

One of the hopes of the future lies with the sea-water magnesia process, in which slaked dolomite and sea-water are reacted with the precipitation of insoluble magnesium hydroxide This process which now supplies the bulk of magnesia for refractories in this country is capable of a wide range of control thus a pre-war content of about 6 per cent calcium oxide has now been reduced to about 2 per cent It has been shown that such material used with chrome ore yields an excellent chrome-magnesite brick for all-basic furnace work

Magnesia still supplies the standard lining for the basic induction furnace[13], though here again there is no evidence of intercrystallization On the contrary, borax and silica are frequently added to the mixture because they promote the formation of forsterite ($2MgO\ SiO_2$) at a low temperature with a volume expansion that ensures steel tightness in the intermediate temperature zones of the lining It would appear that the silica dissolves in the borax forming a glass which then attacks the magnesia grains The solid forsterite formed crystallizes as a shell around the grains thus forcing them apart At higher temperatures the forsterite again goes into solution in the melt and a high firing shrinkage results We are thus presented with the phenomenon that the safest induction furnace linings are usually those which show the worst shrinkage cracking at high temperatures but a small positive expansion at temperatures around 1,100°C

One other development in the magnesite field demands comment the increasing use of unfired basic refractories, not only in steel plants but also in copper furnaces and cement kilns Unfired bricks are now available which under certain conditions give lives equal to those given by fired bricks In other applications severe breakdown occurs, apparently due to loss of strength in an intermediate temperature zone If unfired bricks are heated up in steps of 100C° to top temperature it will be found that in the region above 600°C and below 1,200°C there is a marked loss of strength, the modulus of rupture dropping to about one tenth of the original figure If now the working face is subjected to stress, due for example to the rapid freezing and melting of adhering slag, the stresses set up in the brick may well result in fracture at the weak zone and a consequent loss of the working face. Slag adherence and weak zone formation are then repeated followed by a further loss. Once again the brick is not slagged or melted, it is merely broken off in lumps.

DOLOMITE

Recent progress in dolomite refractories has been in the physical rather than the chemical field. In the early days of the 1939–45 war great strain was thrown on the dolomite bottoms of open hearth furnaces due to air raid warnings. To avoid glare steel was frequently held for long periods on the hearth after it was ready to tap. As a result there was a serious increase both in major repairs and breakouts. An *ad hoc* research committee, known as the Basic Furnace Linings Committee - Technical Panel, was formed to handle this and allied problems and its findings have been published[14].

The first point which emerged was that dense hearths could not be made out of the normal material because this was substantially of one grain size. It was essential to have a continuous grading, such as could be obtained by controlled pan milling. If such a mill is charged and samples taken at intervals for packing density the latter is found to increase in the manner shown in *Figure 5*. It will be seen that in the first mill the packing density rose from 1·8 to 2·5 gm/cm³ in 8 min, whereas in the second and third mills 20 or 30 min were required to achieve a similar result. The effect of grinding on the intergranular porosity is vividly brought out by the shadowgraph shown in *Figure 6*. The adoption of such controlled grinding together with the use of the optimum tar content led to a general improvement in open hearth furnace bottoms throughout the country, and a general swing from burned-in to fully rammed hearths.

CHROME AND CHROME MAGNESITE

Chrome ore as mined consists essentially of a complex spinel of the type $R''O\ R'''_2O_3$ together with varying amounts of gangue. The divalent atom is normally Fe or Mg, and the trivalent Cr, Al or Fe. Comparatively few straight chromite bricks are now made, but there is a substantial production of chrome magnesite bricks. These generally consist of 70 per cent of coarse chromite mixed with 30 per cent fine magnesite.

It is this type of brick that has come nearest to providing an answer to the problem of the all-basic furnace, in which the silica bricks in the top structure are completely replaced by basic bricks. The use of this type of construction has enabled the output of certain furnaces to be increased from 14 to 18 or even 19 heats per week. Furthermore the roof life in one such furnace has improved from 125 to about 360 heats. The thermal conductivity of basic bricks is normally rather higher than for those of silica and hence with similar operating rates the fuel consumptions tend to be greater. If, however, full use is made of the additional safety factor the fuel consumption can be reduced by faster driving to less than that normally obtained with silica furnaces. The only serious objection to the general use of all-basic construction is the high price of chrome magnesite bricks, about six times that of silica bricks. Further improvements will be necessary before all-basic furnaces are generally economic, but the target is so attractive that research is being concentrated in this field and it may not be long before the problem is solved.

A great deal of work on chrome was carried out towards the end of the war

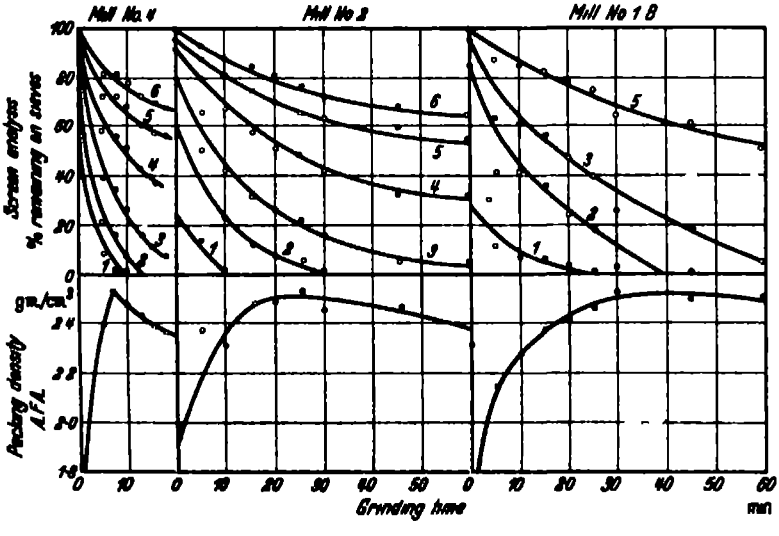

Figure 5 Typical variations of grading and packing density with time, crushing loads mill No 4, 12 tons, No 2, 5½ tons No 1B, 3 tons Note Sieve classification 1—0·5 in, (1 in = 2·54 cm) 2—0·25 in, 3—7 B S S, 4—25 B S S, 5—72 B S S, 6—150 B S S Aperture size 3—2,411 micron, 6—104 micron

By courtesy of Iron and Steel Institute

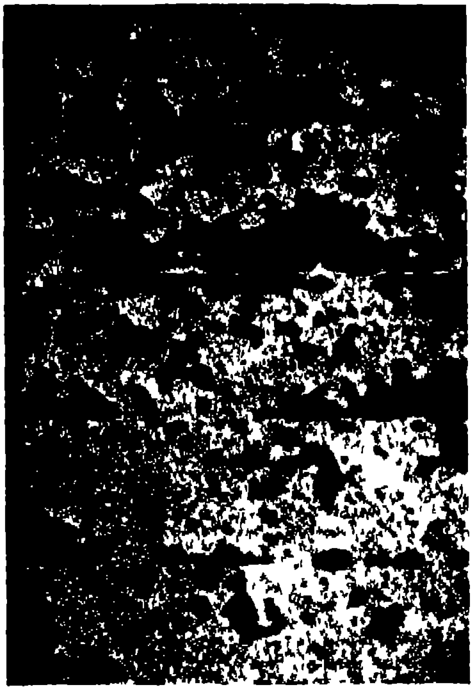

Figure 6 Shadowgraph showing reduction in intergranular porosity with milling time Milling time 0 min 15 min 30 min 45 min 60 min

By courtesy of Iron and Steel Institute

by the British Refractories Research Association and much of this work has since been published[15]

Effect of reducing atmosphere—Chrome bricks frequently grow during kiln firing and in extreme cases may appear like lumps of coke at the end of the firing period In 1945 T R LYNAM, T W HOWIE, and J H CHESTERS[16], following up certain indications from German and American work, showed that some chrome ores, particularly those high in iron oxide, grew very rapidly when maintained between 600 and 800°C in a reducing atmosphere The work of G R RIGBY[16] has since shown that this growth is associated with the breakdown of ferrous chromite to give a solid solution of ferric oxide and chrome oxide, which on subsequent heating in a reducing atmosphere returns to ferrous chromite with a marked volume expansion The changes can be summarized by the following equation

$$FeO\ Cr_2O_3 \xrightarrow[\text{or oxygen above 300 C}]{\text{heat in air}} Fe_2O_3\ 2Cr_2O_3 \xrightarrow[\text{above 700 C}]{\text{heat in a reducing atmosphere}} FeO\ Cr_2O_3$$

chromite spinel, a constituent of chrome grains

solid solution of sesquioxides deposited in chrome grains

chromite

$\downarrow$ *no change in volume*

$\downarrow$ *30 per cent increase in volume resulting in friability*

Bursting in contact with iron oxide—The expansion in reducing atmospheres appears to be mainly a manufacturer's problem due to difficulties arising from the tendency of chrome magnesite bricks to expand rapidly when they absorb iron oxide It is generally agreed that the expansion is associated with the solid solution of magnetite, itself a spinel, in the isomorphous chrome spinel crystals, but just why this should give an expansion when other solid solutions *e g* ferrous oxide in magnesium oxide, do not is by no means clear

It has been shown that certain combinations of spinels are more prone to bursting than others, and that the effect can be reduced by increasing the magnesia or gangue content of the brick So far, however, no satisfactory way of avoiding the difficulty has been obtained, since additions of, say, talc to the brick batch to prevent bursting are liable to lead to a marked reduction in the refractoriness-under-load, which is already below that desired Indeed it is only by suspending either all the bricks in the roof or alternatively the rib courses that any long term stability can be obtained The refractoriness-under-load figure as normally determined is not low, but unfortunately creep tests carried out both in compression and in torsion show that such bricks cannot be relied on to carry a typical roof load above about 1,350°C This means that the first few inches of a roof brick are always soft

ALUMINO-SILICATES

Fireclay bricks are still produced in larger quantities than any other type of refractory A great deal of research is being done not only by refractory technologists but also by soil chemists on the structure of clay itself, but as yet there is no clear answer to certain elementary questions, such as why fireclays are usually more plastic than pure kaolin One of the major problems with fireclay bricks is their tendency to shrink in service and any solution of this problem is complicated by the difficulty of obtaining consistent test results[17] R S BRADLEY and his co-workers[18] have recently suggested a method of minimizing shrinkage in service by the addition of water soluble sulphates *e g* aluminium, ammonium or magnesium sulphate, to the clay batch prior to manufacture

It would appear that the addition of sulphates results in the liberation of sulphur dioxide or other sulphur-rich gas at high temperatures and that, where sufficient glassy material is present to entrap the gas, bloating of the material occurs with consequent compensation of shrinkage

J MACKENZIE[19] has shown that there is a strong correlation between the behaviour of firebricks in blast furnace stoves and the change in their modulus of rigidity when re-fired in the laboratory Strangely enough both the aluminous bricks, which have been hard fired, and the siliceous bricks, which have not been so well fired, show little change, whereas the intermediate alumina brick shows a marked increase in rigidity particularly if high in alkali With the siliceous bricks any increase in rigidity due to vitrification appears to be offset by the more open structure caused by bloating

CARBON

During the last few years there has been a big increase in the use of carbon in iron works in this country and in the United States One reason for the sudden interest is that research work carried out in this country[20] suggests that carbon may provide the answer to two major worries of blast furnacemen breakouts of metal from the hearth and scaffolding in the stack, due to the adherence of material to the stack lining Its use might also reduce the size of the so-called 'bears' or 'salamanders' formed by the freezing of iron in a hearth cavity when the furnace is blown out A study of the cause of breakouts[21] led to the conclusion that they were not just the result of bad workmanship, faulty joints for example, but rather to the oxidation of iron penetrating into the pores in the fireclay brick The zone of maximum oxidation is usually about 1 in (2 54 cm) behind the working face, the ferrous oxide content in this zone rising to as high as 15 per cent Since a fireclay brick with this ferrous oxide content is soft even at 1,300°C it is not surprising that large pieces of the lining come away and the process of wear is repeated Given a mechanically sound carbon lining no such effect would occur since any oxidizing agent penetrating the bricks would react with the carbon to form carbon monoxide, the only result being a slight increase in porosity The entry of large quantities of air or water vapour would of course be fatal because the bricks themselves would disappear, but this should not occur with any well designed furnace

A major advantage of carbon lies in its high thermal conductivity This makes the external water cooling much more effective, any iron attempting to penetrate through the brick joints being immediately chilled Furthermore carbon is inert to almost all the chemicals likely to appear in a blast furnace with the exception of oxygen The principal difficulty in the use of carbon is one of design It is not sufficient for the blocks to be chemically resistant, they must stay in position Fortunately carbon shows only a very slight after-contraction (of the order of 1 per cent) in service, and this can readily be allowed for in any fully keyed or interlocking design The major difficulty is to develop a hearth that will not lift if metal gets underneath it The registered block design shown in *Figure 7* appears to meet t[illegible] requirement and so far has proved entirely satisfactory It will be seen that the bricks are all interlocked both within the course and between courses In the latest installations no attempt is made to get tight joints between the blocks, indeed a substantial clearance is allowed to facilitate installation In general several such courses, amounting in all to about 5 ft (1 53 m) in height, are placed on a refractory concrete base, which in turn rests on the steel sheets used to seal off the bottom of the hearth jacket It is assumed that when the furnace reaches working temperature and molten iron is formed the latter trickles down through the joints probably reaching at least the second or third row of blocks before it freezes In the top courses the iron will remain molten The hearth is held down at the edges by keying under the sidewall and the design is such that even if localized failure of the key structure occurred it is unlikely that more than an odd block or so would float

The second essential is that the side lining should be quite distinct from the central section, it should consist essentially of a carbon chimney that will remain undisturbed even if the central hearth floats With large furnaces this chimney is built up to

Figure 7 Blast furnace hearth section showing interlocking of carbon blocks

Registered design, by courtesy of Carblox Ltd

water-cooled staves and between these and the outer jacket there is a further course of carbon In the unlikely event of the molten metal reaching the stave coolers, spray cooling can be started on the outside jacket and any risk of actual breakout minimized

Carbon is also excellent as a bosh lining In this region between the hearth and the stack there is normally very rapid attack on the fireclay bricks, heavy copper coolers being built in to maintain the bosh lines In recent installations these fireclay bosh linings with their expensive copper coolers are replaced by a simple carbon lining, that may be as thin as 9 in, but is spray-cooled on the outside of the jacket One such installation that has been examined after four years' use was found to be in almost perfect condition, the minimum thickness being about 13½ in compared with the original 13½ in

The use of carbon in the stack is a new and quite recent innovation The problem here is twofold

1. fireclay bricks tend to disintegrate due to the deposition of carbon in the lining
2. fireclay bricks show burden adhesion with consequent formation of scabs or scaffolds on the inside of the lining, which frequently grow to such a size that only half of the original working area is left

Furnace operation is then irregular, output decreases and dust losses greatly increase Tests made in the laboratory showed that of all the ordinary refractories carbon is the only one which does not show adhesion with the burden constituents Small trials were, therefore, made of carbon panels in a stack and these have now been followed by the installation at Appleby-Frodingham of two all-carbon blast furnaces, built without any firebricks whatsoever apart from a ring around the taphole and a few courses in the armouring region at the top of the stack The taphole fireclay bricks were left because of the risk of carbon oxidizing in this position due to air inleakage or steam from the taphole stopping material Those at the top of the furnace were left purely as an economic measure, there being no need for increased durability in this position. It is still too early to say whether the all-carbon furnace will provide a complete answer both to breakouts and scaffolding, but one such furnace has been in operation for over six months and is working particularly smoothly

SUPER-REFRACTORIES

This subject which has recently been discussed by R E Birch[21] really demands a review of its own. Great progress has been made in special refractories for jet engines, atomic energy and other small consumption jobs, but there is still no super-refractory for general use Price is a major consideration and the author agrees with Birch that magnesia, alumina and zirconium silicate, offer the greatest promise of development Much of the recent work on refractories, including that on metal-refractory mixtures (known as *Cermets*) is still confidential, but a fair idea of the field covered can be gained from the literature[22-27] (in particular reference 23) The chief interest to the normal user of refractories lies in the unique properties of certain of these materials As an example it can be stated that sintered alumina, which would be fantastically expensive if purchased in the form of standard squares, has a crushing strength of about 150 times that of a normal firebrick

CONCLUSIONS

The subject of refractories is still new Progress is rapid but the properties of the materials at present available are still poor compared with those theoretically attainable The next few years may well see big improvements now that an increasing number of workers is entering the field

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Colorado Beetle Problem

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POTATOES rank high among the staple food crops of the world and any factor that may seriously affect the yield is of direct economic importance The Colorado beetle is one such factor, it is a major pest of potatoes in many countries and is still extending its range It is an adaptable insect with remarkable powers of multiplication under certain conditions and the prevention of losses due to its depredations constitutes a problem affecting food production on a large scale This insect is therefore a subject worthy of intensive investigation both because of the economic implications of the problem it presents and of its intrinsic scientific interest and, in fact, there is probably no other pest of growing crops that has been studied in greater detail

The adult Colorado beetle is about one centimetre in length, shaped rather like an abnormally large ladybird and conspicuously marked with black and yellow longitudinal stripes on the wing-cases, it can fly well, though long distance flights are unusual The female beetles lay batches of orange-yellow eggs, the grubs, which hatch in a few days, are at first dark brown, later becoming a bright pinkish-red colour with two rows of black dots on each side When fully fed the grubs burrow into the soil, pass through a short resting stage as pupae and finally change into adult beetles which emerge from the soil The winter is always passed in the soil in the adult beetle stage, those which come to the surface in the late summer, burrow down again at the onset of cold weather Both beetles and grubs feed on potato foliage, the tubers themselves being nibbled only if other food is not available If the insects are present in large numbers in the early part of the summer, the foliage may be wholly or partially destroyed with consequent failure or reduction of the crop of potatoes

The Colorado beetle (*Leptinotarsa decemlineata* Say), now so notorious a pest, was at first merely an insect of scientific interest It was originally described by T SAY, who found it feeding on a wild species of *Solanum* (*S rostratum*) when on an expedition in 1824 to the almost unknown region of the Rocky Mountains Some years later settlers reached this area bringing with them the cultivated potato *S tuberosum* The beetles and their grubs found that the potato was even more to their liking than the original host plant and, provided thus with an abundant food supply, they greatly increased in numbers, gradually spreading eastward Severe losses of potato crops occurred and at times great swarms of beetles were reported By 1874 the Atlantic coast of the United States and south-eastern Canada had been reached, and apprehension began to be felt lest the pest should be carried by ship to Europe It was not however until 1922 that the Colorado beetle really established itself in Europe, near Bordeaux, although in the intervening years there had been some isolated outbreaks in Germany and England, which were exterminated by drastic action Since then, particularly during the war when preventive and control measures could not be effectively applied, the insect has spread and become a serious pest throughout most of western Europe as far east as the borders of Czechoslovakia, Poland and Hungary It is not established in England though there have been a number of small isolated occurrences arising from beetles reaching the country by ship with goods from the Continent, the Channel has proved to be an unexpectedly effective barrier to any large scale invasion and the special organization maintained by the Ministry of Agriculture has been able to deal with and eradicate successfully all breeding colonies of the insect that have been found The greatest number, 57, of such attacks occurred in 1947, in 1948 there were 11, and in 1949 not one was reported Continued effort will however be needed if the country is to be kept free from this troublesome pest and the aim is to stamp out completely any colonies that may occur In countries where the insect is an established pest this is not a practicable policy and routine control measures to keep the pest in check must be undertaken

The problem is one of international importance and entomologists in the European countries concerned have long been in touch on the subject In 1936 a European scientific committee for the study of the Colorado beetle* began work and in 1947, on the initiative of the United Kingdom, an official International Committee on Colorado Beetle Control was formed with headquarters in Paris which coordinates and helps to finance operations in the cooperating countries, additional to the normal control measures undertaken

A means of control by the application of Paris Green to infested crops was discovered in the United States at an early stage (about 1865) but it was soon recognized that the Colorado beetle problem demanded not only the urgent investigation of remedial measures for immediate use in the field but also long range scientific studies of the insect. Research on the subject has been undertaken, at first in the United States and Canada and since 1922 in Europe, mainly in France, Germany, Belgium and Holland, to obtain full knowledge of the insect with a view to the improvement of known means of control or the discovery of new methods. The United Kingdom has been unable to take part in such investigations because of a fortunate lack of material, but she has greatly benefited from the published work and helpful cooperation of entomologists in other countries in dealing with the problems arising in the application of preventive measures.

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* The scope of the work of this organization (Comité Européen d Études de Zoologie Agricole) has recently been extended to include other pests of international interest

The literature on various aspects of the Colorado beetle problem is very extensive and only a brief review of some of the work can be attempted here. The chief lines of investigation have been:

1 Studies of the habits, behaviour, biology and general ecology of the insect.

2 Studies of the food plants, and attempts to breed resistant varieties of potatoes.

3 The role of predators and parasites and other natural enemies.

4 Field and laboratory studies of direct control measures, chiefly insecticides, their toxicity to the insect and suitability for practical use.

BIOLOGY AND ECOLOGY

One of the striking characteristics of the Colorado beetle is its ability to maintain itself under a wide variety of environmental conditions[1, 2]. It flourishes best however in temperate climates and extremes of heat, cold, wetness or dryness are unfavourable. Taking its distribution on the American continent as a guide, the area in which it may occur lies approximately between the mean annual isotherms of 0°C and 20°C, thus bringing within its range in Europe both Norway and southern Spain. It is not however likely that it would become a serious pest of potatoes near the extremes of its possible range, and even under favourable conditions the abundance of the insect is markedly affected by seasonal weather and varies greatly from year to year. Temperature is perhaps the most important factor. It determines to a great extent the date of appearance of the over-wintered beetles in the spring, the duration and extent of egg laying, the rapidity of development of the larvae, the movement by flight of the adult beetles and the date at which hibernation begins. Emergence from the soil in the spring becomes general when a soil temperature of 14°C or more is reached at the depth of hibernation, but this is not invariable; some individuals remain in the soil till much later and others after feeding may return to the soil and hibernate over two winters.

Some feeding is necessary before mating, which may take place before or after hibernation. Eggs are deposited most commonly on the underside of the leaves, normally in batches of about 30, though smaller and larger batches are not uncommon. Egg laying continues at intervals during the summer, sometimes interrupted by a resting period, the number laid by a single female varying greatly; 500 to 800 is common, though much larger numbers have been recorded. Under certain conditions, apparently associated with cold and wet weather, a proportion of the eggs may be eaten by the beetles and this curious habit is perhaps one of the factors helping to account for instances often observed of apparently heavy infestations failing to develop seriously. When fully developed within the egg, the young larva cuts its way out with the help of hatching spines formed on the thorax, and its first meal is usually its own egg shell. It then begins to feed on the foliage, undergoing three moults in the course of a larval life of about 20 days, the length varying according to the prevailing temperature. The greatest amount of feeding takes place after the third moult. The larvae are hardy and resistant to unfavourable weather, though heavy rain and wind may lead to high mortality in the young stages; they are sluggish and do not leave the plant on which they were hatched unless driven to do so by lack of sufficient food. The depth to which the fully fed larva burrows for pupation is determined largely by the nature of the soil, varying from 3 to 15 or more centimetres. The pupal stage lasts from 8 to 15 days according to the temperature, the adult beetle then coming to the surface to seek food and a mate. If food plants are immediately available the beetles tend to remain near their place of emergence but they are active and can crawl considerable distances in search of food. Temperatures of 25°C and over stimulate great activity and the insects then readily take to the wing. Flights are normally short, not exceeding a few miles, but under certain conditions, not clearly defined but always associated with high temperatures and often with stormy weather, great numbers may take to flight at the same time and move with the wind over long distances. In the early days in the United States, before adequate control measures were available, such mass movements greatly assisted the rapid spread of the insect. They have also occurred on the Continent leading to the invasion of new territories, and in several instances masses of the beetles have come down into the sea and have been washed ashore on the coasts of Holland and Belgium and in the Channel Islands. The invasion of Switzerland by the pest was largely due to such mass flights carried by high winds from the west. The movement of swarms of this kind has occurred both in autumn and in early summer, in the United States autumn flights, and on the Continent summer flights soon after emergence of the over-wintered beetles, have been the more important

Eggs, larvae of various stages and adults may all be found on the plants at the same time during the summer, as a result of the variable date of emergence and egg laying by the over-wintered beetles Under favourable climatic conditions there may be two or even three generations of the Colorado beetle in the year, but over most of its range one generation in the year appears to be normal When the temperature falls in the autumn the beetles return to the soil for hibernation, burrowing to a depth of 25 to 40 cm or occasionally deeper, they are able to survive very hard winters, particularly if there is a good cover of snow, though mortality from various natural causes is sometimes high during hibernation

From this brief summary of the results of studies of the biology and ecology of the insect it will be seen that attempts to forecast the probability of its relative abundance or scarcity from year to year are beset with difficulties B TROUVELOT and P GRISON in France have given special attention to the differences in the dates of emergence and egg laying under differing climatic conditions in relation to the subsequent intensity of infestation, and because of the great variations observed it is concluded that even local forecasts need to be based on surveys carried out each year None the less such surveys may assist in providing early notice of impending infestations, and a European intelligence service, supplying up to date information concerning the incidence of the pest in different regions, which has been organized by the international committees referred to previously, is proving valuable

FOOD PLANTS

The biological relationships of the Colorado beetle and its food plants are of much interest[9] [11] The insect feeds only on plants in the Natural Order Solanaceae and chiefly within the genus *Solanum* As already mentioned, it transferred readily from the wild *S rostratum* to the potato *S tuberosum* when opportunity offered and it will also feed on Woody Nightshade *S dulcamara*, Black Nightshade *S nigrum*, aubergine *S melongena*, tomato *S lycopersicum* and outside the genus *Solanum*, on Deadly Nightshade *Atropa belladonna* and Henbane *Hyoscyamus niger*

The relative attractiveness of these plants and their suitability for development of the insect differ greatly Potato and aubergine appear to be the most attractive and favoured food plants, development can also be completed on Woody Nightshade and less easily on Black Nightshade, whereas tomato is little attacked under natural conditions even near infested potato fields and beetles feeding only on tomato foliage become lethargic and do not reproduce Petunia, another solanaceous plant, is definitely poisonous to the larvae, they will eat enough to poison themselves when there is no alternative, but the plant is completely ignored if suitable food is available Tobacco is not attacked

Much attention has been given in France and Germany to the possibility of discovering a commercially useful variety of potato unattractive or resistant to the beetle Apparent differences in the extent to which existing varieties suffer from attack have been found to be due rather to the state of growth reached at the peak period of emergence and egg laying in the spring than to any intrinsic property, though a few varieties appear to be relatively less attractive or to withstand injury to an unusual degree

A more promising line of work on this problem has arisen from a study of wild tuber-forming species of *Solanum* which show wide differences in suitability as food plants for Colorado beetle, ranging from species as readily attacked as *S tuberosum*, through varying degrees of susceptibility, to some with definitely resistant properties Adult beetles will feed even on the more resistant species though there is evidence that they are adversely affected, larvae, on the other hand, usually feed very little and fail to develop normally Among species possessing resistant characters *S demissum* is of particular interest Larvae placed on this plant, although they remain on it, appear to lose the desire to feed, they eat scarcely enough to maintain life and development is incomplete or at best slow and irregular It is uncertain whether the foliage has a definite toxic action but recent work in Holland indicates that the effects on the larvae are mainly the result of undernourishment and that death is due to starvation The attractive possibility of producing resistant strains of the potato by crossing *S tuberosum* and *S demissum* is being actively pursued in France and Germany[9] though progress is slow The work is difficult and complicated by the fact that the results vary to some extent with different strains of *S demissum* and individual larvae vary in their ability to survive on the plants Hybrids with some of the resistant characters of *demissum* have been obtained but these characters tend to be lost in the F_1 and F_2 generations on recrossing with *tuberosum* and no hybrid has so far been produced combining resistance with high yields of tubers Experiments are also in progress with another resistant species, *S chacoense*

Little is yet known of the chemical factors determining the differences in behaviour of Colorado beetle larvae when feeding on different species of

Solanum and much fuller biochemical investigations than have so far been undertaken are needed to assist the work of plant breeders

NATURAL ENEMIES

The importance of the natural enemies[37 37] of insect pests as factors affecting their abundance has long been recognized and the subject has been fully studied in relation to the Colorado beetle

The larvae are occasionally subject to a bacterial disease and, more frequently, entomophagous fungi, species of the genus *Beauveria*, are found attacking the adult beetles in the soil In artificial culture, a high mortality among hibernating beetles can be obtained by introduction of the fungi, but under natural conditions neither of these organisms appears to spread readily

Insect parasites of the Colorado beetle are comparatively few Two species of Tachinid flies are occasional parasites of the larvae in the United States and attempts have been made to introduce them into Europe A small hymenopterous egg parasite *Anaphes pratensis* has been found in France and Belgium Neither of these insects however is an important limiting factor

Predatory insect enemies of the beetle are of greater economic interest The most important in the United States are two species of Pentatomid bugs [38-43], *Perillus bioculatus* and *Podisus maculiventris* which attack Colorado beetle larvae, and a Carabid beetle, *Lebia grandis*[44,45], the larvae of which are ectoparasites of Colorado beetle larvae and pupae and the adults predacious on larvae and eggs Locally, these are sometimes sufficiently numerous to play a useful role in reducing numbers The biology and requirements of these insects have been fully investigated and a great deal of work has been done in France and Germany with stocks obtained from Canada and the United States in the hope of establishing them in Europe Breeding of the Pentatomid bugs proved relatively easy but this was not so with the Carabid *L grandis* because of its rather complicated life history However, suitable techniques have been worked out for producing large numbers of all three species under artificial conditions and liberations in infested potato fields have been made in various localities Unfortunately, the relative dryness of the summers in France and Germany has proved a serious obstacle to the introduction of these natural enemies, both *L. grandis* and *P maculiventris* are sensitive to climatic variations and thrive only under conditions of relatively high temperature and humidity Though in some instances they have maintained themselves for short periods after liberation in the open, they succumb easily to unfavourable conditions, and they have not so far been successfully established in Europe

Several species of Pentatomids indigenous in Europe have been found attacking Colorado beetle larvae and two of these, *Picromerus bidens* and *Troilus luridus*, have been studied in detail, chiefly in Belgium There is some hope that these insects may prove useful auxiliaries

Starlings and partridges have been reported to feed on Colorado beetles and their larvae but most birds[46, 47] find them distasteful and, in general, observation on natural enemies of the pest do not suggest that they are likely to play more than a minor part in helping to keep it in check

DIRECT CONTROL

The early work of C V RILEY in Missouri, U S A, showed that sprays or dusts containing Paris Green could be effectively used for control of infestations of Colorado beetle on potatoes and it was this discovery that has led to the development of arsenical insecticides on a very large scale[48 44] Paris Green, though effective, has a number of disadvantages and is now rarely used It has been replaced by lead and calcium arsenates which can be more readily prepared in a form suitable for use as sprays, lead arsenate in particular can be made to give a very fine suspension in water which adheres well to foliage Both these insecticides have for many years been widely employed against Colorado beetle and application of a spray containing 0 5 per cent calcium arsenate has been regarded as the standard means of control on the Continent Barium fluosilicate has been used as a spray or dust to some extent in France and a good deal of attention has been given, particularly in Germany, to the possibilities of killing beetles emerging from the soil after hibernation by means of dressings of calcium cyanamide ' Some success with this treatment has been obtained but results have been variable Insecticides prepared from Derris or Lonchocarpus root, containing rotenone as the chief active principle, have also been found to provide effective control but are less persistent, they have special usefulness under certain conditions, for example in gardens, because they are not poisonous

The range of available insecticides has been extended with the introduction of the newer synthetic organic insecticides, particularly dichlorodiphenyltrichloroethane (DDT) When the insecticidal properties of DDT were discovered in Switzerland early in the war, one of the first insects used for test purposes was the Colorado beetle and it was found that DDT was highly toxic both to the grubs and adult beetles Laboratory and field experiments in many countries later confirmed this and DDT insecticides are increasingly replacing the arsenicals for use in practice, particularly in the United States, Canada, Switzerland and Holland They are also used for preventive spraying in the United Kingdom

Both dusts and sprays containing DDT are employed A number of different types of spray fluids are available and experiments in Holland indicate that DDT emulsions are superior to other forms, particularly with regard to persistence of the toxic action The usual concentration at which the sprays are applied is approximately 1lb of DDT per 100 gallons (99 8 gm per 100 litres) In the United States and Canada 3 per cent dusts are commonly recommended and give good control

Another new insecticidal compound, benzene hexachloride, has also proved to be highly toxic to the Colorado beetle but it is not at present recommended for use in practice because potatoes are particularly liable to develop an unpleasant flavour where this insecticide reaches the soil in which they are grown Experiments with chlordan in America indicate that this new insecticide is also effective for controlling Colorado beetle though it does not appear to have any special advantages over DDT

The present situation with regard to direct means of control of Colorado beetle is thus reasonably satisfactory and serious losses of potato crops in areas where the pest is established can be avoided provided that appropriate measures are regularly taken None the less, no effort should be spared in the endeavour to prevent the insect from further extending its range, since control measures, often involving two applications of insecticides during the season, add appreciably to the cost and trouble of growing potatoes The Colorado beetle is a potential pest almost wherever potatoes are grown and, as with the locust problem, international action is needed to deal with it Much of the recent research work on the subject has been carried out under the auspices of the European scientific committee already referred to, and though its activities were interrupted by the war, they were resumed in 1946 and this body now acts in an advisory capacity to the official international organization for control of Colorado beetle The prospect of further advances in dealing with this difficult problem is greatly increased by the international collaboration thus ensured

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Micromethods in Histochemistry and Cytochemistry

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THE problem of the distribution of enzymes in tissues and cells can be investigated in several different ways One way, and that originally adopted by the histologists, is to make the action of the enzyme visible under the microscope by letting a tissue slice act on the substrate under conditions where a colour is developed or a precipitate formed by the reaction products of the catalytic process (G Gomori[1]) This method is hardly quantitative and, in finer cell structures, considerable doubt will always exist with regard to the identity of loci of enzyme action and loci of maximum colour or deposit of solids

Another, more powerful, method related to the former is to trace the enzyme by its direct absorption of light, ultraviolet, visible and infra-red This principle has been used especially for estimation of nucleic acids (for technique see T Caspersson[2], and A W Pollister and M. J Moses[3]) Its usefulness for enzymes seems to be limited at present as characteristic absorption spectra are usually lacking

A third method of importance especially in cell investigations is to homogenize a large quantity of uniform tissue at low temperature and centrifuge the suspension of matter obtained, collecting samples of different particle sizes and densities An enzymatic analysis of the fractions in connection with methods of identifying their particles with histologically defined structures (granules) of the intact cells may then permit certain conclusions regarding the sites of enzymes in these cell structures (R A Bensley, I Gersh, A Claude and F L Schneider[4-6]) Difficulties due to the redistribution of enzymes during the process of isolating the granules tend to reduce the value of this method

Finally, a fourth method is based on a dissection of cells, preparing and analysing samples of well characterized size and structure, often after a centrifugation of the living cell, to obtain a more unequal distribution of structural elements This procedure requires micromethods for enzyme determination and estimation of sample size Such methods have been developed by the authors but only to a scale which permits analysis of large cells (marine ova, amoebae[7]) or groups of cells (histochemistry) Further refinement of these methods may of course be accomplished but will undoubtedly meet with increasing difficulties as regards manipulation, characterization and measurement of the samples When trying to achieve higher refinement a point will therefore be reached where the quantitative correlation between structure and chemical property can no longer be controlled, and where other methods of attack become increasingly profitable However, the available micromethods have a value in themselves apart from their usefulness in the field of histochemistry and cytochemistry *viz* they may be of help to the biochemist in all investigations where the amount of biological material is small

In what follows only methods of the last mentioned type will be described The treatment will be of more recent developments . Other methods and applications have been published in detail by D Glick[8]

ENZYMATIC METHODS

Titrimetric methods— The methods originally described by the authors[9] have undergone no startling development in recent years A number of different microburettes and stirring devices have been described[8] but the limit of accuracy has not been significantly lowered and manipulations have not become much simpler A series of more recent applications may be mentioned histochemistry of the stomach (A Søfborg-Ohlsen[10], R Rask-Nielsen[11]) , retinal histochemistry (C B Anfinsen *et alii*[12]) , histochemistry of the barley root (H P Bottelier[13]) , saccharase in root tips (H Wanner and U Leupold[14]) , and peptidase in drosophila (E K Patterson, M E Dackerman and J Schultz[15])

Manometric methods— Various manometric micromethods are available today[8] (see also J R Gregg[16]) Of these, we shall describe only the Cartesian diver technique[17, 18], partly because it is the only one with which we have had personal experience, and partly because it is, as far as one can judge from the literature, the one that has been most extensively tested and adapted to different analytical purposes

A Cartesian diver consists of a container, surrounded on all sides by liquid, and enclosing a gas space which enables the diver to float in the liquid If the pressure on the liquid is changed, so is the volume of gas enclosed in the diver, and the diver rises or sinks If, on the other hand, gas is absorbed or liberated in the diver, then a corresponding change occurs in the pressure necessary to bring the diver to rest at a given level , thus pressure can be measured very accurately

Figure 1 shows the apparatus used. In *Figure 2* the diver itself is shown in its simplest form , it is made of thin-walled glass, weight about 25 mg, total volume about 12 µl It has a solid glass tail, the weight of which maintains the diver vertical and is so adjusted that the equilibrium pressure of the diver is a little less than one atmosphere The actual reaction space of the diver is closed with a seal of paraffin oil If necessary, a second seal may be placed below the first one, for example a drop of caustic soda solution for the absorption of the carbon dioxide evolved in respiration The liquid in the flotation vessel is a strong salt solution, usually sodium chloride and sodium nitrate, in which gases are sparingly soluble The flotation vessel is connected with the manometer tube by a capillary in order to make the total volume of air as small as possible The height of water in the U-shaped manometer tube is regulated by means of two pressure regulators, one for coarse and one for fine adjustment The difference between the levels in the two branches of the manometer can be reproduced with an accuracy of 1 mm which corresponds to a measurable volume change of 1×10^{-3} µl for a gas volume of 10 µl in the diver

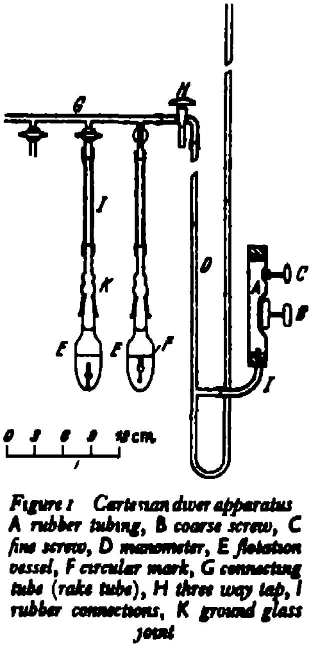

Figure 1 Cartesian diver apparatus A rubber tubing, B coarse screw, C fine screw, D manometer, E flotation vessel, F circular mark, G connecting tube (rake tube), H three way tap, I rubber connections, K ground glass joint

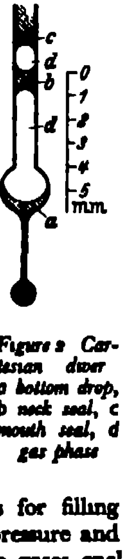

Figure 2 Cartesian diver a bottom drop, b neck seal, c mouth seal, d gas phase

Details regarding the procedures for filling the divers, measuring the equilibrium pressure and calculating the volume changes of the gases enclosed have been fully described elsewhere[18] We shall mention briefly a few recent developments of the technique which have been introduced with the purpose of widening its range of application

One of the main technical problems of all manometric methods is the procedure of mixing two or more solutions after the system has been closed and equilibrium obtained Every one who has worked with the Warburg technique knows the various shapes of vessels that have been devised to meet this requirement. In a vessel of the size of a diver such contraptions are difficult to duplicate and the only principle that can be used is to place small drops of the required solutions on the inside wall of the diver neck (side-drops) and to mix them with the movable neck seals by application of suitable pressure changes In order to keep the pressure changes within manageable limits, however, the distance between side-drop and seal must be small and the danger of premature coalescence is correspondingly great Such a technique has been used by C B Anfinsen and C L Claff[19], and also for years in the Carlsberg laboratory Our own results, however, have never been entirely satisfactory and have therefore never been published Recently, S Schwartz[20] and J C Waterlow and A Borrow[21], by coating the diver wall with silicone, have found a satisfactory solution of the mixing problem

This improvement permits the study of various enzymatic reactions which previously were more or less unsuited to the Cartesian diver technique Among the enzyme determinations of this nature which have been or are being tested the following may be mentioned cytochrome oxidase (E J Boell[22]), amino acid oxidase (S Schwartz[20]), choline esterase (E J Boell and S-C Shen[23], H Holter[24]) To this class of reactions belongs also the determination of the respiratory quotient (E J Boell *et alii*[25], and H Holter[26])

The main parts of biochemical investigations in which the Cartesian diver has been used so far were, naturally, concerned with measurement of respiration These include work by P E Lindahl and H Holter[27] on gradients in embryos, E Zeuthen and K Linderstrøm-Lang[28] on respiration during mitosis, and C A Villee[29] on biochemical genetics in drosophila These are examples chosen in order to demonstrate the applicability of the Cartesian diver to various biological problems (see also J Brachet[30])

Dilatometric methods— Only once, for cytochemical investigations[31, 32], have dilatometric methods been used Since, however, their principle is useful in many respects, the only micromethod in use[33] will be described briefly

The method is based upon a density determination in the so-called 'gradient tube' which is shown in *Figure 3* In the upper bulb there is a mixture of kerosene and bromobenzene of specific gravity 0 99. In the lower bulb there is another mixture of the same liquids of specific gravity 1 01 and in the connecting tube the specific gravity varies linearly from 0 99 to 1 01. The whole system is saturated with water at a suitable vapour pressure If a drop of an aqueous solution is introduced at the top of the tube it will sink through the medium and come to rest in a position where the density of the surrounding medium is identical with its own Hence the density of the medium at any place may be determined provided the gradient is standardized The positions of the drops are measured in a horizontal microscope with micrometer

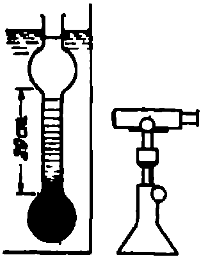

Figure 3 Gradient tube

The use of this apparatus for enzymatic microdeterminations is based upon the fact that isothermal chemical reactions in liquid systems are followed by volume changes which may be used, first, in characterizing the reaction in question and, secondly, as a measure of its progress If therefore a drop (0·1 to 0·2 µl) of reaction mixture (substrate + a piece of tissue or cell) is introduced into the gradient tube it will sink rapidly to an initial equilibrium position, and then move slowly upwards or downwards, according to whether the reaction is accompanied by dilatation or contraction From this movement of the drop the change in density may be determined Constant temperature is a necessary experimental condition

It is beyond the scope of this review to discuss the theory of the volume change With dilute solutions and under constant conditions it is to be expected that proportionality will exist between volume change and chemical change

$$\Delta d/\Delta m = \omega = \text{constant}$$

Of course, the conditions will never be absolutely constant since the reaction itself produces changes, but the above relation is nevertheless usually satisfied It must be emphasized that where ions are produced from neutral molecules (or *vice versa*) ω can show a strong dependence on the conditions of reaction[14] (*p*H, buffer concentration)

Since some 10 to 15 min elapses between the mixing of enzyme with substrate and the arrival of the drop at the level of equal density when the measurement of its movement can begin, the first part of the reaction is missed, a fact which limits the applicability of the method

If the reaction is a zero order reaction the enzyme determination is easy, since the slope of the straight line representing the relation between time and density can be considered a direct measure of the rate of reaction and of the amount of enzyme. The enzyme determination is not a problem with true first order reactions, the enzyme amount simply being proportional to the reaction constant For complicated reactions, however, it becomes difficult to construct arbitrary enzyme unit curves because of the uncertainty of the zero point extrapolation

Colorimetric methods— Several colorimetric methods for enzymatic work have been described[8] and in certain instances there is no doubt that optical methods are superior to all other methods of this type, both with respect to accuracy (*i e* reduction of scale, not relative accuracy) and to simplicity of manipulation

Recent developments in the technique of photoelectric measuring devices have made it possible to perform colorimetric measurements on a microscale The cuvettes that have been described by O H LOWRY and O A BESSEY[15] for use in the Beckmann spectrophotometer are adapted to volumes of 50 µl coloured solution

The arrangement described by H HOLTER and S LØVTRUP[16] requires volumes of only 5 to 10 µl with a light path of 10 mm The essential parts of this arrangement, seen in *Figure 4*, are a microscope, a camera adapter with a side-view eyepiece, and a photocell The cuvette is a glass or plastic cylinder 5 to 15 mm long with a centric bore of 0·5 to 1·5 mm diameter It is sealed on to a microscope slide by means of cement or vaseline, and closed by a cover slip The light beam has a diameter of 0·2 to 0·4 mm and consists of practically parallel rays

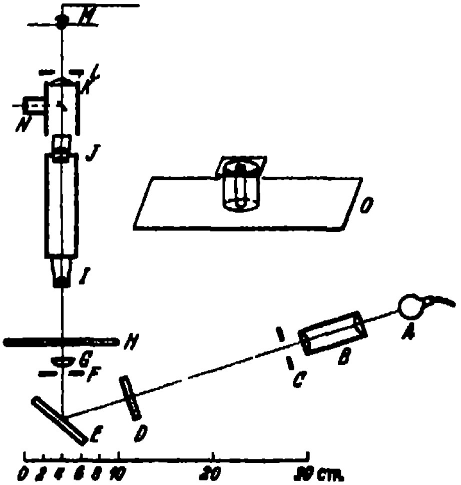

Figure 4 Photometric apparatus A light source, B lenses, C diaphragm, D filter, E mirror, F diaphragm, G condenser, H mechanical stage, I objective, J ocular lens, K photographic adapter, L shutter, M photocell, N side-view eyepiece O cuvette (natural size)

The cuvette is placed on the mechanical stage and centred with regard to the light beam By means of the side-view eyepiece one can control the interior of the cuvette and ensure that no fibres, air bubbles *etc* obstruct the light path Then the shutter of the camera adapter is released and the measurement is taken

This simple arrangement has proved very satisfactory in practice It can be combined with colour filters or with a monochromator B COMMONER[37] in a similar arrangement has used the Beckmann monochromator as a light source

So far the apparatus has been used for the determination of catheptic proteinase in amoeba cytoplasm Casein was used as a substrate and the colour measured was that of the Folin-Ciocalteu reagent[33] E J KRUGELIS[38] has applied the method to the determination of alkaline phosphatase in amphibian embryos

METHODS FOR DETERMINING SIZE OF SAMPLES

The methods to be described here are not only useful in determining the size of samples obtained by microdissection of cells and tissues but also in estimating the size of organisms (amoebae) which are shaped so irregularly that direct measurement of their dimensions does not lead to satisfactory results

Volume— Volume may often be used as a reference quantity *e g* when comparing samples of similar nature In the method devised by H HOLTER[39] the quantity of dye solution displaced by the sample is measured colorimetrically Other methods in which the sample (an organism) is sucked into a thin capillary of known diameter for its length to be measured may be more harmful to the object than Holter's method where a wider capillary is used for the determination of the volume of dye solution + sample

Weight— The most obvious and satisfactory measure of sample size is the weight of the sample, and several microbalances have been constructed[9] that permit a satisfactory determination of weights down to about 0 1 μg The only disadvantage of weighing samples of tissue and cells is connected with the drying of the samples prior to weighing, a process that is difficult to carry out in a quite reproducible way It may therefore cause irreproducible changes in the enzymatic pattern of the tissue Thus it is generally impossible to use the same sample for weighing and for enzymatic analysis, this means that a correlation between weight and enzyme activity can only be found in a series of uniformly varying samples (sections of a regular piece of tissue) where alternate samples can be used for weighing and analysis.

Reduced weight (*R W*)— In the determination of reduced weight (weight of sample — weight of same volume of water) the sample is weighed in water and may therefore be retrieved after weighing without damage and used in enzymatic analysis

Reduced weight may be determined in the gradient tube mentioned, where the positions of aqueous drops with and without sample added are compared Since, however, many enzyme systems are destroyed by the medium in the gradient tube the use of E ZEUTHEN's more elegant method[40, 41] is recommended, this is based upon the Cartesian diver principle

The balance (*Figure 5*) consists of a diver, filled with the flotation medium (culture fluid *etc*) except for one gas bubble which keeps the diver floating at a suitable pressure The air chamber is connected to the outside by means of a capillary which permits the pressure adjustment and which is so fine that diffusion losses are reduced to a minimum One measures the equilibrium pressure of the balance, empty and loaded with the object which is to be weighed, from the pressure difference, R W can be calculated

The balance shown in *Figure 5* consists of a thin-walled glass flask carrying a collar of polystyrene (the balance cup) into which the object is pipetted under water The weighing accuracy is 1 to 3×10^{-8} μg R W, depending on the size of the balance It should be especially emphasized that determinations of absolute weight can be obtained by repeating the weighing procedure in a medium which has been given a different (higher) density by addition of a substance with a high molecular weight such as soluble starch The condition for a satisfactory measurement is that the water balance of the sample is not disturbed by the substance used to change the density The calculation of the weight follows from the equations below

$$(\mathrm{R\,W})_w = g - v d_w$$
$$(\mathrm{R\,W})_{st} = g - v d_{st}$$
$$g = \frac{(\mathrm{R\,W})_w d_{st} - (\mathrm{R\,W})_{st} d_w}{d_{st} - d_w}$$

where *g* and *v* are the weight and volume of the sample, *d* is the density, and the suffixes *w* and *st* refer to water and starch solution respectively The possibility of measuring the wet weight of a sample is of special importance when comparisons are carried out between samples of highly different density In many biological investigations, however, the R W suffices as a measure of mass

H. HOLTER and E ZEUTHEN[42] have shown a use of the balance for purposes other than estimation of sample size in which the changes in the reduced weight of starving amoebae are correlated with their general metabolism

Nitrogen content— A reference quantity of a different kind is the *nitrogen content* which may be taken as a measure of the amount of protoplasm of a sample Nitrogen may be determined by a suitable micro-Kjeldahl method

Among the numerous methods described in the literature[42] and reviewed by D GLICK[8] (see also J SHAW and L C BEADLE[43]), that by D BRÜEL, H HOLTER, K LINDERSTRØM-LANG and K ROZITS[44] claims the highest accuracy (0 005 µg nitrogen) and is probably also the most elaborate one Apart from the reduction of scale it deviates from the macro-Kjeldahl (by which is meant here the 20 mg nitrogen method[45]) with respect to the following points

1 the digestion is carried out with copper sulphate, potassium sulphate and selenium as catalysts (1 µl sulphuric acid) ,

2 distillation is carried out in vessels coated with paraffin or, recently, silicone (*Figure 6*), diffusion and convection being the causes of transfer of ammonia from the bottom drop to the receiving seal ,

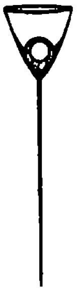

Figure 5 The polystyrene-glass balance

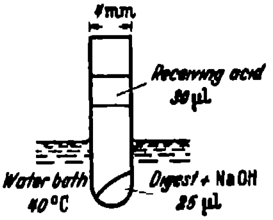

Figure 6 Distillation vessel

3 base is added to the receiving seal in slight excess and the solution is titrated while in the distillation vessel with N/100 hydrochloric acid using a 50 µl microburette and bromcresol green as indicator A glass bead with iron and a magnet[9] are used for stirring

Details of certain manipulations involved in the process of transferring the acid digest from the digestion vessel to the distillation vessel will not be mentioned here We should like however in this connection to emphasize the general usefulness of some of the plainer tools in these microdeterminations *e g* the semi-automatic pipettes with construction shown in *Figure 7* and the braking pipettes for transferring organisms shown in *Figure 8* (see also C L CLAPP[46]) The semi-automatic pipettes have been found to deliver amounts of liquids down to 1 µl with an accuracy of about 0 1 per cent and to empty themselves more completely, relatively, than macropipettes of 1,000 times their volume They are therefore recommended for microchemical work in general

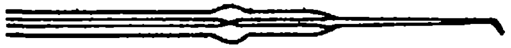

Figure 7 Semi-automatic pipette The liquid is measured off between the upper construction and the tip, and the pressure in the pipette [applied by a pressure regulator] is adjusted so that the pipette empties itself when the tip touches the liquid or the glass wall

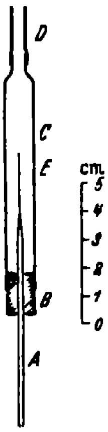

Figure 8 Braking pipette A pipette, B cleft cork, C jacket tube, D rubber tubing, E brake By suction at D the organism may be drawn slowly into A, the fine capillary E serving as an air brake

In the Kjeldahl method the samples are lost, and whenever it is important that nitrogen and enzyme activity be determined in the same sample the latter quantity must be estimated first, which is only rarely possible It may then be possible to apply the ingenious Engström method[47] to dry sections or smears of tissue or cells prior to enzyme analysis In this method the absorption of x-rays of specific wavelengths is used as a measure of the number of nitrogen atoms in a given volume The absorption of a sufficiently broad x-ray band may also be used to measure the mass of a given sample (total mass of atoms irrespective of type[48]) and the method is therefore also an extremely sensitive ' microbalance ' It remains to be seen how detrimental this measuring principle is to the enzymes of the samples, but irrespective of a possible enzyme destruction the method possesses great advantages in that it increases the sensitivity of the determination of mass and of individual elements by several powers of ten

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Forest Research Institute

M NASLUND

Director of the Forest Research Institute, Stockholm, Sweden

The Forest Research Institute of Sweden was founded in 1902, and from a rather modest beginning has grown considerably to attain its present size The greatest development took place in the years 1912 and 1944 The Institute constitutes the central organ for government supported forestry research in Sweden

The Institute has two main functions One is to ascertain how the forests should be most suitably managed under various conditions, and the other is to maintain a running inventory of the country's forest resources and the changes occurring therein In order to fulfil these functions the work is carried out by six departments the forestry, forest survey, operational research, botany and soils, genetics, and the zoological division In addition to these there is a department for mathematical statistics

Research at the Institute is based primarily on the analysis and study of experimental data collected on field surveys Therefore the field work is very extensive and this is carried out on some thousand regular experimental plots and temporary investigation plots, scattered over the whole country In addition to these the Institute has at its disposition four experimental forests with a total area of 3,400 hectares (about 8,160 acres) of forest land, as well as a genetics experiment field of about 500 hectares (1,200 acres)

The aim of the experimental parks is twofold first, to concentrate a number of experiments in a carefully selected and examined area and secondly to study the effects of measures for forestry conservation with application on a large scale

Results of the activities of the Institute are published by various means, such as Reports of the Forest Research Institute, special pamphlets, technical journals, and lectures and practical demonstrations

FORESTRY DIVISION

The research of the forestry division concerns silviculture and forest mensuration

The central task of this division is to provide a practical method of solving the primary questions of silviculture These problems can be divided into two groups, one concerning the management and care of the stands and the other concerning re-generation The scientific methods which are developed to offer practical solutions to these problems are based on production research and re-generation research

The task of production research is to find ways of deciding on the type of tree, pure or mixed, whether the stands are to be of the same or various ages, the time for the first thinning and the length of the thinning intervals, the strength of the thinnings, high or low thinning, thinnings with a view to quality, the time and method for final cutting of the stand *etc* The importance of this branch of research however, extends even further The organization of the forestry industry and the appraisement of the forests is also greatly dependent on the results of production research

In the field of international forestry experimenting, investigations have long been carried out to determine the development of stands and the production of various classes, with the application of one or another method of management (or in exceptional cases even several) The material has consisted of experimental plots which have been cared for over a long period of time according to the method in question The analysis has been accomplished through simple graphic comparisons of their long periods of development

The Swedish Forest Research Institute has, for several reasons which will not be mentioned here, abandoned these methods of experiment and set out in general to determine the manner in which the tree and the stand grow under various natural conditions and with different types of management This expanded aim has led to problems which can only be solved through mathematical-statistical methods

The work within the production research department is carried out in the first place on the basis of observations of short periods of development which are set up as statistical functions These latter serve to generalize the observations and in this way allow a calculation of the increment of growth when this is not known.

With the aid of such an increment of growth function, together with certain other functions, production tables can be set up which reveal the development of the growth, the production, and the harvest for various combinations of the conditions

The data available up to the present have been compiled from the Institute's experimental plots The first of these was laid out in connection with the founding of the Institute almost 50 years ago, and the others have been added successively through the course of years The material, which was gathered according to an older method of experiment and not with the aim of statistical analysis, has been found to be impaired by great deficiencies for its present purpose, causing many difficulties in analysis. For this reason a collection of samples was begun in 1941 for a great production investigation according to the new principles The collection of material from virgin forests has now been completed, and the project is to be continued in stands which have been thinned

The new production investigation, which is based on a single observation of temporary experimental plots, the trees of which are examined for the increment of growth of the diameter by means of borings, and which covers pine, spruce, and birch forests, as well as mixed coniferous and hardwood forests, aims further, however, than the facilitation of production planning The careful examination with respect to the habitat and quality of the tree of a large number of experimental plots, where the increment of growth is known, provides a deeper insight into the conditions necessary for growth A simultaneous consideration of the environment and the race ought to make it possible to separate their respective effects through statistical analysis The material gathered from the virgin forests also enables a study of the influence of the changes of climate on the production

In connection with the new production investigation, the Institute is also studying, in cooperation with the Swedish Forest Products Research Laboratory, the technical characteristics of the development of the forests, as well as their dependence on natural conditions and on the management of the stand

The programme being handled by the forestry department for research on forestry mensuration is carried out in direct connection with the production research, and includes continual development of the method for the mensuration of different trees, as well as the volume of the stand, class of wood produced, and the increment of growth Pruning measures are also being studied with the aim of improving the quality of the growing forest

The new production investigation mentioned earlier includes only the main types of trees, pine, spruce, and birch The production of oak, beech, ash, and other more important types of trees is studied in special investigations

The task of re-generation research is to find the most suitable method for the re-generation of the forests and to give directions as to the applications of the various methods of re-generation

Concerning natural re-generation, problems arise as to the most suitable method of re-generation cutting, the care of clearings, the most desirable time, the way and the costs for the carrying out of plant weeding, consideration of the quality and type of the trees at weeding *etc* In this connection questions of the necessity for such measures as mechanical and chemical screefing, burning *etc* also present themselves

In order to solve the main problems of natural re-generation it is essential to know how the forests are re-generated under various natural conditions and with different types of management This aim is achieved by the Institute through statistical methods, applied to observations of the condition of re-generation or of short periods of its development In this way it is possible by means of functions or tables to reproduce the process of re-generation from the time for the beginning of the liquidation of the old stand to the development of the young forest in the soil The results of re-growth with various kinds of re-generation cutting can in this way be compared under conditions otherwise equally natural, and thus an objectively based decision can be made as to the various types of re-generation programmes

The need for deeper insight into the biological conditions of natural re-generation is taken into consideration through observations concerning the characteristics of the re-generation and the mother stand, the soil, the climate, the seed formation *etc*

In the field of forestry cultivation a great number of problems arise concerning the care of seedlings, the choice between different seeds and methods of planting with respect to biological and economic viewpoints, the development of such new methods, practical problems of fertilization, the characteristics and treatment of plant materials, the amount of spacing between plants, the most favourable time, the method and the costs for the carrying out of weedings, the most suitable form for individual care during the seedling stage, the race and source of seeds, attacks of disease and many others

To solve the most important problems of forestry cultivation the possibilities of sowing and planting in various forms and under various natural conditions must be known With this aim in mind experimental plots are laid out, arranged according to modern principles of field experiment techniques Because of the statistical analysis which is thus made possible, these experiments attain a wide range Investigations of questions as to the costs of plantation and the implements for forestry cultivation comprise an important part of the research programme In this connection new paths have been opened for the purpose of reducing the costs of plantation through experiments on the mechanization of forestry cultivation work (tractor power)

Since the quality of the sowing is of decisive importance to the results of the forest's cultivation, research concerning the characteristics of the cones and seeds, and concerning suitable management and storage, is of particularly great importance for the forestry industry Moreover, an ever increasing service is required for the benefit of the general public in the gathering of cones and seeds

DIVISION FOR FOREST SURVEY

The main task of this division is to estimate the extent and character of Sweden's forest resources, which is carried out through national forestry surveys Due to the fact that repeated surveys are made at equal intervals (about 15 years), it is even possible to ascertain roughly the changes which take place in the period between the surveys In this way a check on forest conservation throughout the country can be obtained Through cooperation with the production research in the forestry division it is also possible to predict the quantities of timber which should be removed for the most rational management of the forests Such calculations are of great importance for the forestry and wood industries

The first National Forest Survey of Sweden was carried out during the years 1923 to 1929, and was preceded by an experimental survey of the province of Varmland in 1911 The survey of Värmland later served as a model for the Norwegian and Finnish national surveys as well as that in Sweden The second national survey, which was initiated in 1938, is based on the same principles, but increased attention to details in observations and greater precision have been developed

The survey reports separately on State forests, other public forests, corporation-owned forests, and private forests In southern Sweden the last named group has been divided into two categories, according to areas greater than and less than 200 hectares (480 acres) of forest land The condition of the forests and their management within the various groups can be shown in this manner

The collection of material in the national forestry survey takes place in regularly distributed survey belts and sample plots The survey belts and sample plots are laid out along parallel lines, which are marked out by a compass at equal distances from each other, so called survey lines In the survey belts, which in the northern provinces have a breadth of 10 metres and in southern Sweden of 20 metres, the distribution of the area into various types of land such as agricultural land, forest land, swamp, mountains *etc* is taken into consideration, while at the same time the forest land is divided according to the classes or types of trees, the development of the stand, its composition *etc* In the northern provinces the trees are also recorded in the survey belts In southern Sweden this has been limited to the sample plots, which are instead laid out more closely together In the sample plots, which comprise small parts of the survey belts distributed at equal distances from each other, a more detailed description of the ground and the forest stand is carried out, in which certain sample trees are registered and examined with regard to factors which are determinant for the volume, the quality, the increment *etc*

Since the procedure of surveying is in its nature a probability calculation, we can use the methods of probability calculus to determine the distance which is required between the survey lines and the sample plots to attain the desired degree of accuracy in the results of the survey This distance has been chosen for each province so that the total supply of timber within each province is calculated to be estimated with a standard error of 1 5 to 2 0 per cent In the northern provinces the line distance varies between 6 and 10 kilometres (3 6 to 6 miles) The data which are collected in the national survey are also utilized for various special investigations, which are carried out for government authorities, committees and institutions

OPERATIONAL RESEARCH DIVISION

The operational research division was started in 1949, with the object of directing forestry work in all its forms in the most economically favourable manner, at the same time taking into account social conditions As a result of the great variety of circumstances which surround the felling and transport of timber in different parts of the country, general rules as to how this work ought to be carried out can only be formulated to a limited extent Instead, the organization of the work and techniques is normally suited to a limited individual area of forest land and this necessitates a constant check on locally changing needs and their consequences from a technical and economic viewpoint By systematic comparison of work organization and techniques in various sections of the country it ought to be possible to obtain valuable information on the application of different methods, and thus new ideas for improvements can be attained Within this field of investigation are also included questions on the costs for removing timber of unusual dimensions, or of changing the methods of assorting the timber

The primary research of this division includes the following

1 wear and tear which occurs in the use of cutting and chipping tools (saws, axes *etc*) in forestry work
2 study of equipment and mechanical aids, as well as
3 investigational methods

The research within the first category aims at clarifying the theoretical course of events which take place during various methods of operation, as well as defining through careful measurements the quantities and types of power which occur during an operation, the optimum rate of cutting *etc* In the case of hand tools the possibilities for selecting the rate and power of cutting are especially limited, and therefore in this field it has been found most suitable to assume the normal amount of power which a human being is capable of producing The tools can then be designed so that this power is used to the greatest advantage In the use of mechanical aids, such as power saws, for example, there is a greater opportunity for designing the methods of operation with respect to the optimum degree of technological effect

The selection of equipment and machinery with regard to ease in handling, durability *etc* and also investigations on transportation equipment constitutes the second category of the research programme in this division

Closely connected with these studies is the research into methods of manual labour, which is granted a position of great importance in the forestry industry, since it forms the foundation for a generally recognized need for systematic craft training among forestry workers If research on methods of working is to lead to decisive results, however, physiological relationships must be carefully considered and this aspect is therefore dealt with by this division

DIVISION FOR BOTANY AND SOILS

Research in the division for botany and soils covers scientific forestry investigations in geobotany, soil botany, mycology and plant physiology as well as related subjects

The main task of this division is to increase our knowledge of the natural scientific conditions for forestry production This work is therefore particularly directed at determining the often very complex processes which take place in the soil and trees A tree's production is determined by *inter alia* the resources of water, food substances, light, and warmth, which together form the tree's ecological environment But in the forest the environment is affected, in addition to the basic characteristics due to location, by the competition of other trees and living things and the plant community Therefore it is of the greatest importance to examine not only the requirements of the trees and the qualities of the location, but also life and the living things in the soil of the forest, as well as the types of forest-plant communities, their soil requirements and their reactions

The various fields of work of this division can only be defined in broad outline in the analysis of this difficult problem In a forestry ecology experiment, for example, the environment of the forest is varied by different types of operations, such as thinning, watering, or fertilising Resulting deviations can add knowledge as to the level of the food substances and the competition in the soil, and also as to the position of the type of forest on the food substance scale, the requirements of each kind of plant, and the conditions for production of the forest Experiments of this sort are in progress in different parts of the country

In the geobotanical field experiments are carried out on the plant communities of the forest, and particularly on the relation between the different types of such plant communities (types of forests) and the characteristics of the location The type of a forest serves as a very useful indicator in the practical forestry industry in judging the soil and its qualities important for forestry management in a simple manner Geobotanical research is directed towards testing and as closely as possible establishing the value of the types of forests for this purpose

The task of soil biology research is to examine the biological processes important for forestry which are taking place in the soil In general the only method of increasing the amount of food substances available for the soil is to improve the relation between supply and demand of food substances by appropriate felling and by preparing the soil for most favourable living conditions It is therefore the task of forestry soil biology to gather information on the organisms in the soil, their activity, their requirements, their effect on each other and their effect on the roots of the trees

Up to the present time this research has mainly concerned itself with the question of how the food substances can be liberated from the storehouse of the soil In the long run, however, it must be just as or perhaps even more important to determine how quickly the supply of food substances of the soil can be renewed Upon this question depends the answer as to whether or not the forests can be kept growing well in the future without risk of quickly exhausting the food supply of the soil Great and arduous labour still awaits soil biology research here

The mycological section concerns itself with research on the fungus diseases of living trees as well as on the injurious diseases which attack the forestry products and with the development of methods whereby the damaging effects of fungi can be overcome

The effects of snow blight *Phacidium infestans* which at certain heights in the northern parts of the country constitute a serious hindrance to the re-growth of pine have been extensively investigated Attention has also been directed toward diseases in the plant nurseries Root rot *Polyporus annosus* which has viciously attacked stands of spruce in certain parts of the country, and pine blister rust *Cronartium asclepiadeum* are also the object of investigations

Storage rot in the lumberyards of the pulp factories is receiving considerable attention, and in co-operation with the zoological division investigations are under way seeking to discover the relation between insect attacks and the occurrence of log blue Field experiments with impregnated timber are being carried out in various parts of the country in conjunction with state authorities to determine the effectiveness of different types of impregnating materials

Research on natural rot fungus poisons in wood, so-called antibioticas, has been carried out within this division for several years in cooperation with the Department for Organic Chemistry of the Royal Institute of Technology, and has been considerably expanded lately

GENETICS DIVISION

Research in this division which began its activities in 1948 covers plant-breeding of forest trees especially based on selective methods, and questions relating to this field

The main task is concentrated around the very complex problem of the influence which the genetic structure of the tree exerts on the production of the forests The characteristics of the tree are always conditioned by both heredity and environment Their mutual importance can be established in different ways The individual genotype of the tree can be determined through vegetative propagation by cuttings or graftings, which are set out in different types of environments, for example in different spacings of plants The value of the progeny can be tested in various manners by sowing the seed obtained after open pollination, after artificial crossing, or after self-fertilisation Only the two latter methods are completely satisfactory from a genetic viewpoint

In connection with the above mentioned investigations, which aim at ascertaining the breeding value of different trees and stands of trees, a national register is being compiled of all pine, spruce, and birch trees, which have been chosen because of their particularly outstanding qualities, such as their high

growth ability, to be used in future breeding work The number of trees selected amounts to 2,500 or 3,000

Sweden's total requirement of coniferous seeds is calculated to amount to about 60 tons per year At present not even half this quantity can be produced In order to cover this shortage, as well as to increase the quality of the stands, various research workers have proposed that special seedling plantations be set up Valuable trees, belonging to a certain provenance region, are propagated through grafting, brought to early blooming and cross-bred in special plantations This plantation method, carried out in the right way, will be of invaluable service to the Swedish forestry It is the purpose of the genetics division to study these and similar problems in special model plantations

In the progeny experiments, as well as in other culture experiments with progeny of different trees and races of trees, the differences of the progenies as regards the resistance to attacks of parasite fungi and injurious insects are studied In cooperation with the entomological and mycological investigators of the Institute, special experiments are being planned for the further study of variations in power of resistance

From the earliest years of the Institute experimental activity has been carried out as to the importance of the origin of seeds, or in other words the geographical races of forest trees, which is known as provenance research This work is now being done by the genetics division It is of great importance to be able to indicate the limits within which seeds of the forest can be transferred without imperilling the result of the culture Also it must be ascertained whether or not through systematic transference of seeds between various latitudes or between tracts with different climatic conditions advantages can be gained in the quantity and quality of the production in comparison with stands grown from local seed

ZOOLOGICAL DIVISION

The animal life of the forest includes many different kinds of animals injurious and useful, insects being the most numerous, both in number of sorts and in total number Insects also play a much greater part than other living animals in the forest from an economic point of view For these reasons the zoological division concerns itself mainly with problems which arise from the occurrence of and damage caused by these insects

One of the main tasks of this division is to investigate the living habits of the insects under various conditions Particularly important in this respect are biological and ecological investigations of two of our most dangerous bark beetles the pine beetle *Blastophagus piniperda* and the eight dentated bark beetle *Ips typographus* Extensive information about the biology of injurious insects is of great importance, since it will reveal under which conditions of development a certain injurious insect has the least power of resistance and can therefore be most easily combated

Suitable methods are also devised for the estimation of the numerical strength of insects, as well as the extent of damage which they cause These estimations are necessary in order to judge to what extent combative measures ought to be applied to minimize damage by insects

The most important task of the division from an economic point of view is to devise effective measures, both preventive and directly combative, which are applied to the respective living habits of injurious insects

Another important problem is the relation between certain injurious insects and injurious fungi It has been shown that some forest insects infect the trees or timber with spores of injurious fungi For instance, certain bark beetles infect timber of pine and spruce with fungi which causes a dark discolouring of the sapwood, known as log blue

Studies of the animal life of forest soil are also carried out, and these provide a wider knowledge of the types of animals found in the forest, as well as their meaning to the soil processes

Among current research projects is included the modern process of spraying or dusting by air with contact poison, which was used for the first time and with good results against the dangerous pine moth *Bupalus piniarius* In this case an insect poison was used which had a nerve crippling effect (DDT) with the help of which extensive areas of forests were completely freed from these injurious larvae in a very short time

DEPARTMENT FOR MATHEMATICAL STATISTICS

The application of statistical methods, particularly regression and variation analysis, to the problem of advanced forestry research has had most successful results Therefore a special department for mathematical statistics has been set up to serve the various divisions of the Institute with statistical analyses of experimental results

Besides the close cooperation between the various departments of the Institute, contact is also maintained with other scientific institutions, as well as the practical forestry industry

Forum: Mathematics in the Larger Context

WHILE agreeing with H W TURNBULL[1] that primal analysis may be as applicable as the usual punctual one in the realm of form and growth, it is possible that readers who are interested in the concept of 'anti-Euclidean' space may not have come across two books[2] that deal with it

Anti-Euclidean geometry is just as derivable from projective geometry as Euclidean is Analogously to defining affine geometry by specifying an absolute plane at infinity, we can define a wholly dual anti-affine geometry by specifying an 'absolute point at zero' Anti-Euclidean geometry is then obtained by specifying an imaginary cone at this absolute zero, a direct perspective of the Euclidean imaginary circle in the plane at infinity This sets up a polar relation between lines and planes in the point, just as Euclidean geometry sets up its dual in the plane

In terms of a continuous transition we can pass from a hyperbolic to an elliptic metric in two ways, the first of which consists of expanding the absolute quadric surface with real radius into the infinite plane, followed by contraction of the absolute quadric with imaginary radius Here we pass through parabolic (Euclidean) geometry Or, secondly, we can contract the real quadric into a point, and then expand on the imaginary side The geometry of the limiting point is, of course, the anti-Euclidean one

Or again the finite real absolute quadric gives rise to two non-Euclidean hyperbolic spaces, not just one Inside the absolute sphere we have a punctual space (like a distortion of the Euclidean), and outside, a primal space WHITEHEAD[3] calls these space and anti-space For an infinite radius, we have all space , for zero radius, we have all anti-space

L LOCHER[2] gives an axiomatic treatment of anti-Euclidean geometry (particularly in Part II), as well as a good number of theorems , he also makes a few speculations about possible applications to science G ADAMS and O WHICHER[2] deal with the application of anti-space to living plants The authors write with almost religious fervour, and engage in what seem to be fairly wild speculations A botanist, in fact, might well throw his hands up in horror, but to my non-botanical eyes the book contains some stimulating ideas

B PASCAL made a pun which is quoted[4] by L DE BROGLIE and which seems very applicable to the section on DUAL HYPOTHESES

'Par l'espace, l'univers m'engloutit et me comprend comme un point par la pensee je le comprend'

As far as my own interests go, I am beginning to wonder about the applicability of primal geometries to optics

F J ZUCKER

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REFERENCES

[1] TURNBULL, H W *Research* 3 (1950) 197
[2] LOCHER, L *Urphaenomene der Geometrie*, I and II Zurich, 1937
ADAMS, G and WHICHER, O *The Living Plant* Stourbridge, Worcs, 1949
[3] WHITEHEAD, A N *Treatise on Universal Algebra* Sect 202 Cambridge, 1898
[4] DE BROGLIE, L *Research* 2 (1949) 102

Miscellaneous Notes

BIRTHDAY HONOURS

THE list of honours includes the following

Knights Bachelor—

Dr A N DRURY, F R S , Director, Lister Institute of Preventive Medicine , Dr N B KINNEAR, lately Director, British Museum (Natural History) , Dr J I O MASSON F R S , Vice-Chancellor, Sheffield University , J E MYERS Principal, Manchester College of Technology

K C B —

Sir BEN LOCKSPEISER, Secretary, Department of Scientific and Industrial Research

THE ROYAL SOCIETY

Under the Statute of the Royal Society which provides for the election of persons who either have rendered conspicuous service to the cause of science or are such that their election would be of signal benefit to the Society, Dr G M TREVELYAN, O M , C B E , has been elected a Fellow of the Society

UNIVERSITY APPOINTMENTS

Birmingham— Professor E A PEEL has been appointed Professor of Education and Head of the Department of Education

Heriot-Watt College, Edinburgh— Professor H B **Nisbet** has been appointed Principal, and Dr I A **Preece**, Professor of Brewing Chemistry

Ibadan, Nigeria— Professor W **Hamilton Whyte** has been appointed Director of the Institute of Social and Economic Research at University College, Ibadan, and will take up his duties in September 1950

Leeds – Dr F S **Dainton** has been appointed to the Chair of Inorganic and Physical Chemistry

Leicester— H P **Moon**, lecturer in charge of the Department, has been appointed Professor of Zoology

Manchester— The Council has appointed M J **Lighthill** as Bizer Professor of Applied Mathematics in succession to Professor S **Goldstein**, F R S

St Andrews – H G **Callan** has been appointed to the Chair of Natural History which has been vacant since the death of Sir D'**Arcy Thompson**

Southampton— A N **Black** will succeed Professor T R **Cave-Brown-Cave**, C B E, as Professor of Engineering

NATIONAL RESEARCH COUNCIL OF CANADA

Laboratory tests on beet molasses have shown it to be such an excellent raw material for the *Cutanedrol* production by fermentation with *Bacillus polymyxa* that the work is being carried to the pilot plant stage Good results have also been obtained with *Aerobacter aerogenes* and *Pseudomones hydrophyla*, yields being close to the theoretical limits Most of the difficulties in purifying waste sulphite liquor before fermentation have been overcome With organic salts and an organic stimulant this medium also produces high yields of diol

THIRD WORLD PETROLEUM CONGRESS

The Congress will be held in the Kurhaus, Scheveningen, Netherlands, 28 May–6 June 1951 Four lectures are to be delivered by speakers of international reputation The lecturers and subjects will be J J **Broeze** 'Future aspects of the applications of fuels and lubricants', C **Hugel** 'Récents progrès dans la chimie du petrole et de ses derives', G M **Lees** 'The oilfields of the Middle East', E V **Murphree** 'Benefits from research to the Petroleum Industry'

CORRECTION

We have been asked by the author, H **Holter**, to state that during shortening of the article 'Laboratories of the Carlsberg Foundation' for publication, p 278 of our last issue, two names were inadvertently omitted, these are Dr **Albert Fischer**, Director of the Biological Institute of the Carlsberg Foundation, and Dr A **Vedel Taning**, Director of the Marine Biological Laboratory at Charlottenlund

COMING EVENTS

First Microchemical Congress, Graz, Austria, 2–6 July

4th Plenary World Power Conference, London, 10–15 July

International Conference on the Properties of Semi-conducting Materials, The University, Reading, 10–15 July

Seventh International Botanical Congress, Stockholm, 12–20 July

Joint International Council of Scientific Unions Commission on Radioactive Standards and Units, Paris, 17–18 July

Fifth International Cancer Congress, Paris, 17–22 July

XVIth International Congress of Opthalmology, London, 17–26 July

Sixth International Congress and Technical Exhibition of Radiology, Royal Horticultural Hall, London, 24–28 July

Fourth International Congress of Soil Science, Amsterdam, 24 July–1 August

International Anatomical Congress, Oxford, 25–28 July

New Books

Die theoretischen Grundlagen der analytischen Chemie

G HAGG (*Translated into German by* H BAUMANN *from fourth Swedish edition*)

(*197 pp, 25 illus, 8 tables, 9¾ in by 6¾ in*)

Basel Verlag Birkhauser, 1950 S *Fr* 18 00 or 22 00

Professor Hagg's work was written to fill a gap in books available to university students in Sweden Treatment of the subject is similar to that in a number of standard texts on analytical chemistry though the omission of reference to details of analytical procedures enables the author to gain greater emphasis in his treatment of the theoretical basis of the subject It is based on the Bronsted conception of acids and bases, together with solubility and redox equilibria The underlying physicochemical principles are clearly stated and, in the later chapters, are applied to such familiar problems of qualitative and quantitative analysis as neutralization and precipitation reactions, the properties of precipitates, complex formation and redox titrations It is regrettable that no references to original papers are given A book of this type is unlikely to be of any great use to English students, but it should interest teachers of analytical chemistry A particularly useful feature is the employment of a logarithmic concentration scale in diagrams showing neutralization and precipitation processes A number of valuable numerical examples are also given at the end of each chapter

H J Emeléus

An Introduction to Photo-elastic Analysis*

A W HENDRY

(*viii + 172 pp, 77 illus, 7¼ in by 4¾ in*)

London Blackie and Son Ltd 1948 7s 6*d* net

There has long been a need for a concise but comprehensive and up to date introductory textbook on photoelastic analysis—a need which has now been met With no previous knowledge of photoelastic technique anyone proposing to install an industrial photoelastic laboratory would do well to read this elementary exposition of the subject He would find there basic optical theory, a clear description of how photoelastic fringe patterns are produced, methods of measuring fringe orders, descriptions of the various forms of compensators, methods for separating the principal stresses, use of the membrane analogy for determining $P + Q$ (denoting the principal stresses at any point) throughout a plane model, a discussion of the most common types of polariscopes and of photoelastic technique, a survey of photoelastic materials and their properties, a short description of the 'stress freezing' method, and, finally, a useful bibliography for further study A clear and adequate exposition is given of the harmonization process for numerical solution of Laplace's equation This purely analytical process for determining the values of $P + Q$ throughout the interior of a plane model is rapidly growing in favour because it requires no additional measuring apparatus and—more important still—involves no experimental errors other than may occur in the fringe pattern With this method and the membrane analogy ready to hand one would not dream of using lateral extensometers which are so sensitive to temperature fluctuation

Somewhat surprising is the omission of reference to the Tardy method of compensation, in which rotation of the analyser to produce extinction gives the fractional fringe order with good accuracy, using monochromatic light The high accuracy† which can be achieved by this method when using a photometric method of observation has been described

The author appears to have been misled by the fact that common bakelite is a phenol-formaldehyde product Although bearing the same trade name, photoelastic bakelite (*BT 61–893*) bears no chemical relationship to the phenol-formaldehyde resins, being actually a glyptal polymer *Fosterite*, which is said to be a generic name for copolymers of organic acids and diethylene glycol with styrene and the announcement of which in the U S A holds out great prospects for three dimensional analysis, is not mentioned

The book is well illustrated, with photographs, diagrams and sketches, and is written in simple language, with an absolute minimum of mathematics

W A P Fisher

Encyclopedia of Chemical Technology, Vol II

Edited by R E KIRK and D F OTHMER

(*vii + 915 pp, illus 10½ in by 7¼ in*)

New York Interscience Publishers Inc 1949 $20 00
London Interscience Publishers Ltd 1949 140s

This volume deals with Anthrone to Carbon Arc and the whole work will be completed in ten volumes The encyclopaedia reflects largely American practice and most of the references are to American journals but a comprehensive summary is given of industrial chemical processes and products with reference also to the equipment employed in the manufacture of chemical products

By accident of its alphabetical sequence, this work contains a number of articles dealing with medical compounds, such as anti-anaemia preparations, antibiotics, antiseptics, antispasmodics, bile constituents, blood albumin, blood fractionation and blood plasma There are also several unusual headings such as anti-freezes, dry batteries, bearing metals, brake linings, building materials and cable coverings but these are adequately considered from the viewpoint of the chemical engineer and chemist

Treatment of subjects varies between different authors of whom there are over 100 contributors to the present volume Thus, in some subjects, the historical background is given in some detail, but it is left out or incomplete in others There are fewer of the flow diagrams illustrating industrial processes which were such a valuable feature of the first volume, and thus the article on antibiotics does not give any diagrams and relatively few details of the industrial processes used in their manufacture, but these will probably be given in later volumes dealing with such products as penicillin and streptomycin

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* See also p 298 of this issue

† Brown A F C and Hickson V M *Improvements in Photoelastic Technique obtained by use of a Photometric Method* communicated to the Seventh International Congress of Applied Mechanics London, 1948

These volumes compare favourably with Thorpe's *Dictionary of Industrial Chemistry* and Ullmann's *Encyclopaedia der technischen Chemie* They have a much more industrial outlook than the former and include much information not given in the latter although in general the treatment is not so systematic as Ullmann The volumes are well produced with a large number of illustrations, and will be an essential part of the equipment of all chemical laboratories of any standing

F H Garner

Hematin Compounds and Bile Pigments Their Constitution, Metabolism and Function

R LEMBERG and J W LEGGE

(*xxvi+750 pp, illus, 9 in by 6 in*)

New York Interscience Publishers Inc 1949 $15 00
London Interscience Publishers Ltd, 1949 120s

This fine book covers the immense field of haematin compounds and bile pigments with a remarkable ability and comprehensiveness After a brief introduction there follows thirteen chapters devoted to methods of investigation, porphyrin chemistry, haematin compounds, haemoglobin and its comparative biochemistry, haematin enzymes, bile pigment formation and other irreversible alterations of haemoglobin, metabolism of haemoglobin in the body, bio-synthesis of porphyrins and the place of pyrrhol pigments in evolution The bibliography contains references to over 3,000 original papers and textbooks Such an encyclopaedic enterprise might well have degenerated merely into an exhaustive and undiscerning compilation , *per contra,* the authors have in nearly every chapter effected a really critical and readable synthesis of existing knowledge up till 1946 (and in some cases up till 1948) Furthermore they have on many occasions interspersed new ideas and suggestions of their own, which not only stimulate the reader at the actual time at which he reads the book but may well influence his research fruitfully for years to come Though the standard of all the chapters is high, particular mention must be made of those dealing with porphyrin and haematin chemistry, and with the metabolism of these compounds and of haemoglobin in the body For many years the work of R Lemberg and his school has been devoted to these difficult problems and to the reviewer's knowledge no comparable review on these important topics has previously been available in English

In their preface the authors justly observe that ' in textbooks of biochemistry and physiology the subject is rarely treated with the care which its importance demands. Perhaps because of the lack of a suitable monograph serious errors are frequent, hypotheses of doubtful value are given as facts, and there is a time lag of many years, sometimes of decades, between the present day knowledge available and that summarized in the textbooks ' Their own monograph is certainly pre-eminently fitted to repair these deficiencies

Misprints and minor errors of fact are commendably rare, though in such a giant undertaking it would be humanly impossible to avoid occasional slips Thus *e g* on p 323 the *p*H of the erythrocytes is given as about 7 4, which is, in point of fact, the normal figure for the plasma, the *p*H of the erythrocyte being about 0 2 unit more acid A more important matter is the proportion of space devoted to the various topics Here there is, of course, room for many opinions, but some readers would have welcomed a fuller discussion of the modern magnetic and electron chemistry work, at the expense perhaps of some of the pages devoted to oxidation-reduction potential

The book is as a whole well printed and attractively produced, but unfortunately the very high price will almost certainly place it outside the scope of many workers in biology, physics chemistry and medicine who would wish to own it Present day costs of production no doubt necessitate such prices, but also raise the serious question whether some means ought not to be found of relieving the researcher's pocket of the cost of essential textbooks, which are really as much the tools of his trade as are the apparatus and laboratory services, for which he does not normally have to pay

In conclusion the authors are to be congratulated on a classical achievement and an outstanding service to their scientific colleagues in many different fields

F J W Roughton

Interplanetary Flight

A C CLARKE

(*viii+164 pp, 15 illus, 7½ in by 5 in*)

London Temple Press Ltd 1950 8s 6*d*

At the present time, when popular journals and the popular press present feature articles on the coming conquest of space with a monotonous regularity, A C Clarke's short but authoritative manual is a wholesome corrective to the wilder imaginations Writing as an ardent propagandist for the cause of space travel, he is commendably honest in his appraisal of the difficulties to be overcome As he points out, a single-step chemical fuel rocket could not possibly escape from the earth owing to the limiting maximum velocity (limiting both by reason of the temperatures and pressures involved and by the very nature of chemical fuels) of around 9 km/sec The utilization of atomic energy for interplanetary flight is even more hazardous and unlikely—the twin problems of cooling and size seem conclusively unfavourable The author's suggested solution is a composite one, involving use of chemically fuelled 'tug' rockets to reach orbital space stations a few hundred miles up, and the construction, actually in space, of atomic powered giant vessels for the subsequent interplanetary journeys He does not dwell sufficiently, perhaps, on the fantastically difficult engineering problems involved here That he is aware of them, however, seems clear from a passage on p 122 The suggestion that rocketry may be to astronautics as ballooning was to aeronautics and that the answer may somehow lie in the deeper understanding of gravity itself removes the whole question of space flight back to the realm of unsupported theorizing

C S YOUD

Fatty Acids and Their Derivatives

A W RALSTON

(ix+986 pp, illus, 8½ in by 5½ in)

New York John Wiley and Sons Inc, 1948 $10 00
London Chapman and Hall Ltd, 1948 80s net

THE subject matter dealt with in this book embraces considerably more than its title signifies Not only are the naturally occurring fatty acids dealt with, but also those which have been obtained synthetically either from the naturally occurring acids or by formal syntheses The higher normal hydrocarbons, alcohols, and dibasic acids in their appropriate sections have, for the purposes of this monograph, been considered as derivatives of the fatty acids, a factor which greatly amplifies and enhances the scope of this book

The chemical properties of the acids are described in detail and an exceptionally well written chapter deals comprehensively with their structure and physical properties

The preparation of the fatty acids from naturally occurring fats, including a review of the intriguing problem of the mechanism of fat hydrolysis, is adequately dealt with and data are given for the characterization of a considerable number of acids by the usual derivatives, and also by some more novel though certainly not less useful compounds

The chemical and physical properties of the simple alkyl esters, glycol esters, and synthetic glycerides, together with amides, substituted amides and amines, the anhydrides, acid chlorides, aldehydes and ketones, the alcohols, their esters, ethers, mercaptans, sulphides, and sulphonates, and the metallic soaps, are all described, though not in the above order, with equal thoroughness

The addendum is essentially a brief review of advances which occurred during preparation of the book Specific references to newer syntheses of olefinic and polyethylenic acids would have been welcomed, as also would have been reference to the elegant contribution of Buu Hoi and associates to the chemistry of compounds exhibiting antileprocidal activity

Developments of **FARMER's** theory for the mechanism of autoxidation and the later contributions to the study of the mechanism of addition of hydrogen to polyethenoid systems might have been quoted

These minor criticisms in no way detract from the value of such a well documented book which shows clear evidence of the author's careful choice both of subject matter and arrangement, and of careful proof-reading It should certainly be available to all those whose work entails any contact whatsoever with the fatty acids and their derivatives

M L MEARA

Books to Come

Geochemistry K RANKAMA and T G SAHAMA (*900 pp, illus, 9½ in by 6¾ in*) Chicago, U S A University Press $15 00, London Cambridge University Press 112s 6d

Physical Aspects of Organic Chemistry W A WATERS (*552 pp, illus, demy 8vo*) London Routledge and Kegan Paul Ltd 35s net

Introduction to the Calculus of Variations C FOX (*264 pp, 53 illus, demy 8vo*) Oxford Clarendon Press 15s net

Theorie des Mehrfachschusses H BRANDLI (*c 250 pp, c 130 illus*) Basel Verlag Birkhauser *c S Fr* 35 00

Biological Studies with Polonium, Radium and Plutonium *Edited by* R M FINK (*404 pp, illus, 9 in by 6 in*) New York and London McGraw-Hill Publishing Co Inc $3 75 or 32s

Propagation of Plants F J KING (*264 pp, illus, demy 8vo*) London Hutchinson's Scientific and Technical Publications *c* 18s

Gastroscopy the Endoscopic Study of Gastric Pathology, *second edition* R SCHINDLER (*xx+458 pp, 374 illus, royal 8vo*) Chicago University Press, London Cambridge University Press 150s net

Handbuch der Laplace-Transformation I Die theoretischen grundlagen der Laplace Transformation G DOETSCH (*c 500 pp c 30 illus*) Basel Verlag Birkhauser *c S Fr* 60 00

RESEARCH SUPPLEMENT

Formation of Munroe Jets and their Action on Massive Targets

W M EVANS, M Sc, Ph D and A R UBBELOHDE, M A, D Sc

The use of 'hollow charges' has been discussed in explosives technique for many years[1-13] but, in spite of suggested practical applications of the phenomenon, very little was known about their real nature Basic research was initiated in the United Kingdom around 1941 to form a background to various applied developments[*] The growth of a few fairly simple experimental concepts stimulated the development of physical theories of the effects

THE CONCEPT OF MUNROE 'JETS'

Bare hollow charges— One of the simplest forms of hollow charge is a cylinder of explosive detonated from one end, and with a hollow, usually a figure of revolution, at the other end (*Figure 1*) The depth

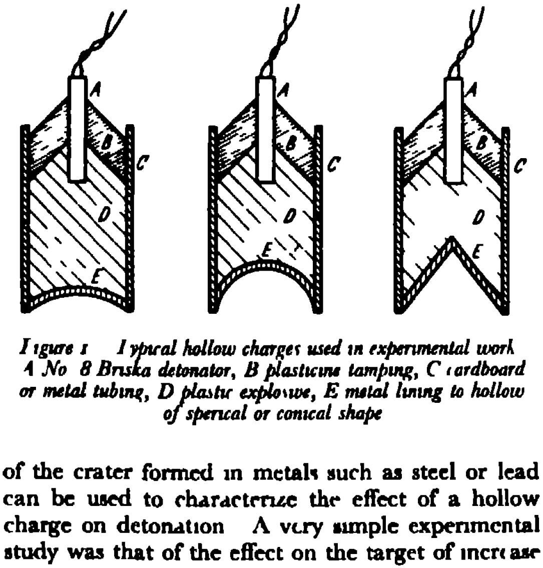

Figure 1 Typical hollow charges used in experimental work A No 8 Briska detonator, B plasticine tamping, C cardboard or metal tubing, D plastic explosive, E metal lining to hollow of spherical or conical shape

of the crater formed in metals such as steel or lead can be used to characterize the effect of a hollow charge on detonation A very simple experimental study was that of the effect on the target of increase of distance between charge and target With a bare (or unlined) flat ended charge, a gap of as little as 25 per cent of a charge diameter (see below) suffices to reduce the effect to about 30 per cent of its former value (*Figure 2* curves *3* and *4*) With bare hollow charges, rapid decay was again observed, though certain characteristics such as crater depth[†] reached a maximum when the base of the hollow was a small distance from the target (*cf Figure 2* curve *2*)

This very rapid decay made it difficult to attribute the effects specifically to the very high pressures or very high temperatures of the products of detonation, except on the assumption of very rapid cooling as the products moved away from the explosive

In addition, it was not clear whether the maximum effect (*Figure 2*, curve *2*) near the base (or end) of the charge was to be attributed to some form of focusing of the products of detonation from the hollow analogous to the focusing of plane light waves by a reflecting surface of revolution

Hollow charges lined with metal— When the hollow was lined with a thin layer of metal the volume of the crater produced was larger than that produced by the unlined charge Characteristics of the crater,

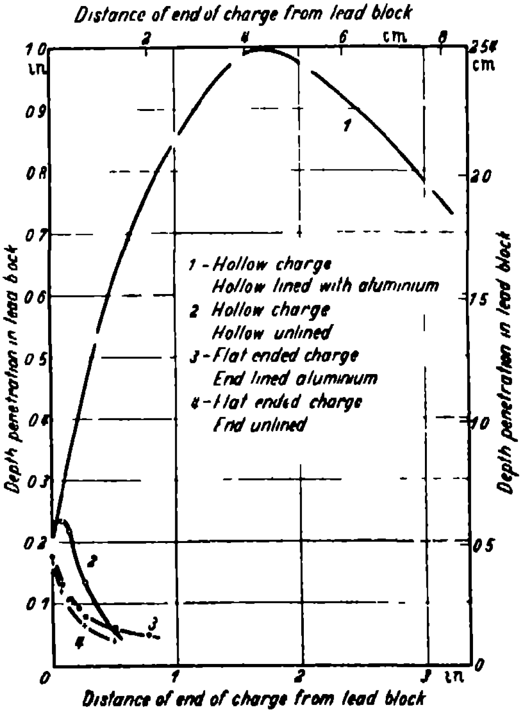

Figure 2 Axial damaging effect in lead blocks of small charges with shaped ends as measured by depth of crater

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[*] Persons particularly associated with some of the work reviewed in this paper were D G Pack, W W Rees and G E Roberts

[†] See also EVANS, W M and UBBELOHDE, A R Some Kinematic Properties of Munroe Jets, *Figure 1* *Research* In press

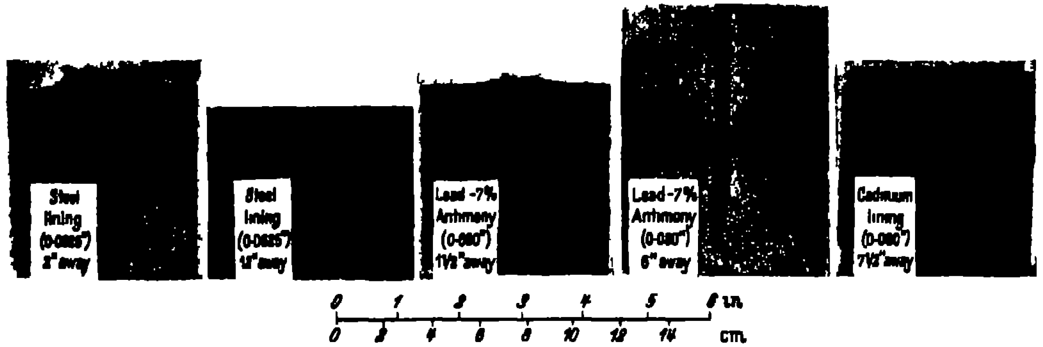
Steel lining (0·0085") 2" away
Steel lining (0·0085") 12" away
Lead -7% Antimony (0·080") 1½" away
Lead-7% Antimony (0·080") 6" away
Cadmium lining (0·080") 7½" away
0 1 2 3 4 5 6 in
0 2 4 6 8 10 12 14 cm

Figure 3 *Sectioned mild steel targets illustrating the characteristic craters produced by jets from charges with shallow hollows lined with metals of high and of low boiling point and fired at various stand-offs*

such as depth, reached a maximum at a considerable distance from the base of the charge and comparatively large penetrative effects persisted over many charge diameters (*Figure 2*, curve *I*)

This suggested that on detonation of the explosive the metal lining formed some kind of projectile which persisted in space after the products of explosion had been dissipated, and which was the agent of penetration, as could be observed by its presence all over the surface of the crater Whether it was acting like a tongue of hot dense gas, or in the form of solid or liquid particles moving with high velocity remained to be discovered The temperature of the metal arrested in the crater would undoubtedly be raised to a high value by impact

To test for the vaporization characteristics of the projectile a series of metal linings of ascending boiling points was used The effects were found to depend to some extent on the shape of the hollow (see below) With a shallow hollow (*Figure 1*) it was observed that a metal of low boiling point such as cadmium, zinc or lead + antimony leads to a penetrating finger-like projectile, whereas a metal of high boiling point such as iron leads to a ' blunderbuss ' effect (*Figure 3*) This gave rise to the suggestion that on detonation of the explosive the material lining the hollow was formed into a kind of jet With a lining of cadmium, for example, the jet might be composed of a stream of dense vapour, and with iron, of a stream of fine fragments The gaseous jets from bare charges would have a much lower density than cadmium jets, but otherwise would be similar

This experimental concept of Munroe jets largely emancipated further research from the rather mysterious ' hollow charge effect ', leaving for further study the problems of how the jets were formed, how they behaved in travelling through space, and how they acted on various materials with which they came into contact

MODE OF ACTION OF JETS ON MASSIVE TARGETS

Metal targets— The supposition that the jets acted by eroding the crater material, in the way that water from a hosepipe could dissipate a heap of sand or an oxy-hydrogen flame rapidly melt away a steel plate, was disproved by a simple experiment The weight and volume of steel targets were determined before and after attack by jets, from which it was clear that negligible losses of target material occurred due to crater formation, thus showing that erosion was negligible , the jets merely pushed aside the material (*Table I*) For targets of low boiling point it was clear that erosion did play a part whether by vaporization or by local fragmentation on impact due to low strength

This pushing aside of target material is fundamental to the action of Munroe jets By measuring the hardness of mild steel in a section cut through a target in which a crater had been formed it could be verified that almost all the hardening by cold working was due to the displacement of target material normal to the axis of the crater (*Figure 4*)

Stopping powers of different materials— By arranging for a given type of jet to penetrate various thicknesses of a range of materials, before encountering the mild steel on which they rested, the remarkable result was obtained that the stopping power of ' fluid ' materials such as water and beeswax was as much as one third that of mild steel Furthermore, freezing water to — 70°C produced an insignificant increase in its stopping power

Thus it was evident that the primary action of ' solid ' target materials like mild steel on the jets did not differ in kind from the action of fluids This was later elucidated theoretically by the explanation that the pressures exerted by Munroe jets are so high that most materials behave plastically, at least to a first approximation In the last stages of crater

Table I Comparative Target Damage from Different Metal Linings (Shallow Hollows) 50 gm charges in cardboard tubing 1 1 in (2 8 cm) diameter (Figure 1)

	Lining	Target				
Test No	*Material gm wt*	*Material*	*Mass change gm*	*Volume change cm³*	*Crater volume cm³*	*Erosion estimated from wt loss*
1	None	Mild steel	0 17	0 15	0 2	1%
2	9 71 iron	do	1 74	0 15	5 2	Not detectable
3	4 39 copper	do	1 88	0 97	4 4	do
4	3 42 tin	do	0 37	-0 01	5 3	9% (max)
5	5 54 lead	do	0 28	0 20	4 8	3% (max)
6	4 07 cadmium	do	-0 62	0 50	5 0	3% (max)
7	7 30 copper	do	6 75	—	2 5	Not detectable
8	8 14 lead	do	0 31		2 8	3% (max)
9	7 89 cadmium	do	0 09		3 3	3% (max)
10	3 70 aluminium	do	-6 85	-0 77	3 3	44%
11	3 49 aluminium	do	4 40	0 24	3 0	20%
12	1 06 aluminium	do	-7 10	0 60	2 9	31%
13	04 aluminium	Cadmium	21 56	(1 5)	9 1	30%
14	Aluminium detonator with *No 8 Briska* used as hollow charge	Lead	0 16	0 01	0 87	Not detectable
15	Copper detonator as hollow charge	Lead	0 15	0 02	0 39	Not detectable

formation the strength of the material is however found to play a controlling part

MECHANISM OF FORMATION OF MUNROE JETS

Change of shape of jets in space – By detailed observations on target damage at different distances (called 'stand-off') between the hollowed base of the charge and the target, it was established that most jets change their shape as they travel through space, probably because of velocity gradients in the various parts of the jet

For effective jet formation it was essential to postulate the collapse of the metal lining Filling the hollow in the charge even with fluids such as water completely inhibited jet formation from all shapes of hollow If the axis along which the jet would form were blocked within the hollow *e g* with a narrow steel pin, jet formation from the deep conical linings was again largely prevented Such prevention of jet formation was much less marked in the hemispherical and shallow hollows, which indicated different mechanisms of formation for conical and spherical linings

Observations on targets showed that the major process of collapse of the metal lining appeared to be complete in a distance of 1 to 2 charge diameters from the base of the charge depending on the shape of the hollow and the thickness and nature of the metal lining Beyond this distance the jet continued to change as it travelled through space, but its formation was not prevented by 'blocking' the path with massive targets These deductions were confirmed later by x-ray flash radiography

Effect of shape of hollow on the formation of jets With most deep hollows whether conical or in the form of spherical caps (depth/aperture greater than about 0 4) the nature of the metal made much less difference to the jet characteristics than it did for shallow hollows (*Figures 5* and *6*) For shallow hollows (*cf* also *Figure 3*) various results strongly suggested

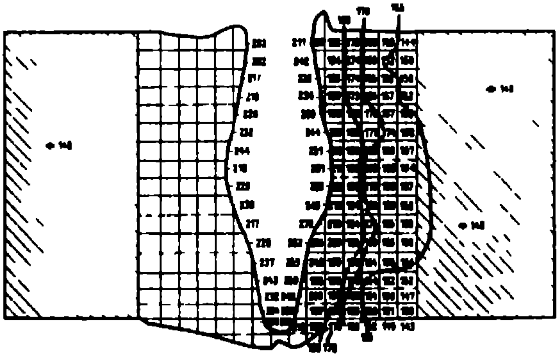

Figure 4 Hardness chart (V P H) of sectioned steel block penetrated by hollow charge jet

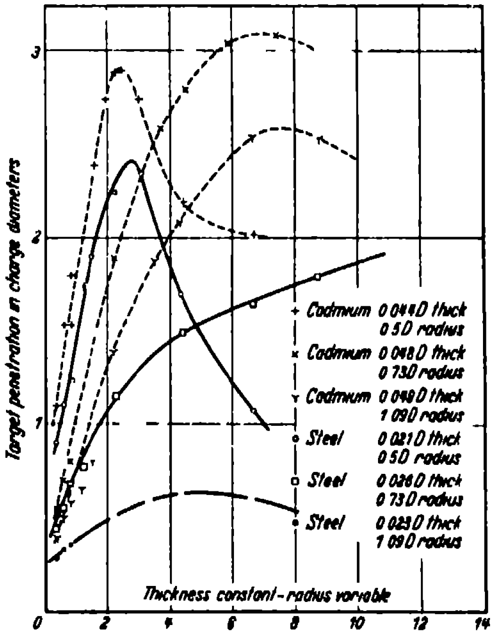

Figure 5 Typical penetration/stand-off curves for various spherical liners (mild steel target)

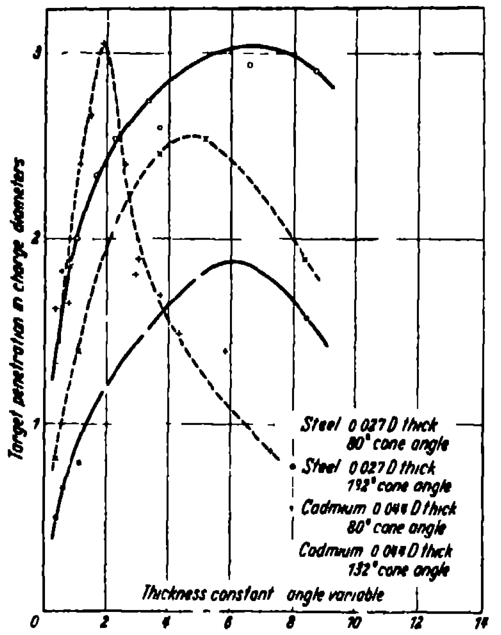

Figure 6 Typical penetration/stand-off curves for various conical liners (mild steel target)

that the soft metals of low boiling point broke up into very fine particles as a result of the detonation, and that the cloud of metal had many of the properties of a dense narrow jet of vapour with high energy, and with high penetrative characteristics On the other hand, metals of high boiling point and high strength gave much broader and less penetrating jets It appeared that the fragments into which the lining broke up followed more or less completely (according to their size and mass) the gas flow imposed by the curvature of the hollow

By firing these jets into soft materials such as ice or solid carbon dioxide the fragments were collected after melting the ice or carbon dioxide and were submitted to physical and chemical examination, including x-ray analysis Metals such as cadmium apparently 'vaporized' completely Linings of mild steel gave fragments of various sizes, including spheres approximately 0 4 to 0 1 mm in diameter, and there was abundant evidence of nitriding and carbiding of the surfaces of these and larger fragments The concept of the jet derived from such experiments was that of a sequence of fragments which interact chemically and thermally with the detonation products With metals of low boiling point such as cadmium this interaction is so extensive that vaporization results, but with steel only the smaller fragments become completely molten in the jet

For deep hollows, particularly cones, although much fine fragment material was collected there was always evidence of a more or less massive plug, the formation of which has been explained in terms of the 'squirt' theory of jet formation[14]

It seemed likely that there were two distinct modes of formation of Munroe jets—the deeper conical hollows giving 'squirts' of high velocity, and the shallow hollows, particularly when spherical in form, giving jets which depended much more on the gas flow following the fragments of the lining

Particulate linings composed of steel fragments of very small size should be able to follow the gas flow much more completely than the larger fragments from a continuous steel lining Tests with shallow hollows lined with a paste of steel filings of average particle size 10^{-6} gm/particle and 10^{-3} gm/particle respectively gave narrow jets similar to jets from cadmium linings Examination of the effect of the gaseous detonation products on such pre-formed steel fragments showed abundant evidence of interaction with the hot gases, and were very similar to the effects observed with the smaller fragments from a continuous steel lining

Shallow spherical caps tilted at an angle θ to the axis of propagation of detonation along a cylindrical charge showed a marked difference of behaviour depending on whether the metal broke into very small fragments (cadmium) or into larger fragments (steel) With cadmium 'fanning out' of the jet occurred whereas with steel the jet remained approximately normal to the axis of rotation of the hollow (*Figure 7*) after allowing for rotation of this axis through an angle φ given by

$$\sin\theta/\sin\varphi = u/V$$

where u — velocity of detonation and
V — velocity of the projected fragments composing the jet u/V was found approximately equal to 3 for both steel and cadmium

With cadmium the jet axis was rotated in the same sense, but in addition the jet was distorted as if the detonation products continued to deflect the cadmium for some time after the initial impulse

EXPERIMENTAL DETAILS AND RESULTS

The experimental details in the work described involved the use of comparatively simple apparatus and techniques

Explosive charges— The main features are illustrated in *Figure 1* *No 8 Briska* were the most powerful commercial detonators readily available With their use in charges of the kind depicted, reproducibility of results in successive experiments could generally be obtained to about ± 5 per cent To promote uniform initiation, a tamping of plasticine was pressed down on to the rear of the charge, about 25 per cent by weight of the mass of explosive used Where it was desirable to avoid damage from fragments of the casing, the charge casing was of cardboard soaked in bakelite varnish and baked However, larger effects were obtained from a given mass of explosive when the casing was of steel To secure uniformity, lengths were sawn from large batches of seamless tubing drawn from the same batch of steel Commercial tubing as used for steam and gas fittings was also used The ratio weight of charge/weight of casing was normally about 0 48 save in special experiments

The various metal linings of deeper form were pressed from metal sheets in one or more stages in hand presses, using very carefully shaped moulds The shallow linings were formed by pressing on to a steel sphere (ball bearing) and shearing off by a steel cylinder *e g* a 3 in (7 6 cm) sphere for a 2 in (5 1 cm) diameter cylindrical charge In a few experiments machine turned metal linings were used

Typical thicknesses of lining used varied from 0 027 *D* for steel to 0 068 *D* for aluminium (*D* — one charge diameter as unit of length) Simple centring devices were employed to ensure good alignment of charge case with the axis of the metal lining, which was pushed firmly against the plastic explosive so as to secure good contact with all parts, with no airgaps

Targets— Steel targets were normally cut from mild steel bar, 3 in diameter, selected so as to be free from core For special purposes stacks of mild steel slabs of about 6 in (15 2 cm) square section were used since it was found that the penetration was not significantly different from that in a corresponding solid target When required, targets of other metals such as cadmium, lead or aluminium were normally cast into steel tubing The aim generally was to approximate to ‘ infinite targets ’ For this purpose, the length (and where necessary the diameter) of a target was progressively increased, in successive experiments with any particular set-up, until further increases made no more difference within experimental error to the effects observed, such as crater depth, crater volume, and crater diameter Methods of measuring these effects and of weighing the targets presented no special difficulty save where allowance had to be made for the material lining the hollow charge when this stuck in the crater

In investigating the stopping power of materials other than steel, such as water, ice, beeswax *etc* the appropriate substance was usually cast or filled into a light steel cylinder immediately in contact with a steel target, so that the residual damage in the steel after the jet had passed through the material could be assessed Special experiments showed that a much larger lateral extension of material gave substantially the same effects This is due to the short time involved in the passage of the jet during which lateral disturbances in the target cannot travel very far

Collection and examination of fragments— For these experiments the jets from 1 38 in (3 5 cm) charges were fired into deep steel cylinders 8 to 10 in (20 3 to 25 4 cm) in diameter containing a sufficient depth of ice or solid carbon dioxide so that the bottom layers were untouched The recovered fragments were examined by standard metallurgical techniques

Mounting of the charges— Owing to the very short time involved in the detonation of the charges and the formation of the jets, comparatively light wooden structures could be used for mounting the charges at the appropriate distances from the targets Most charges were fired vertically they were merely placed on the target, the appropriate stand-off being achieved by three light supports or by cardboard tubing Special experiments showed that mountings with much greater inertia made no difference to the results

Notes— Exact calculation of the percentage erosion when this is small depends on exact evaluation of the weight of lining sticking to the target The figures quoted in *Table I* are estimates of the upper limit of loss

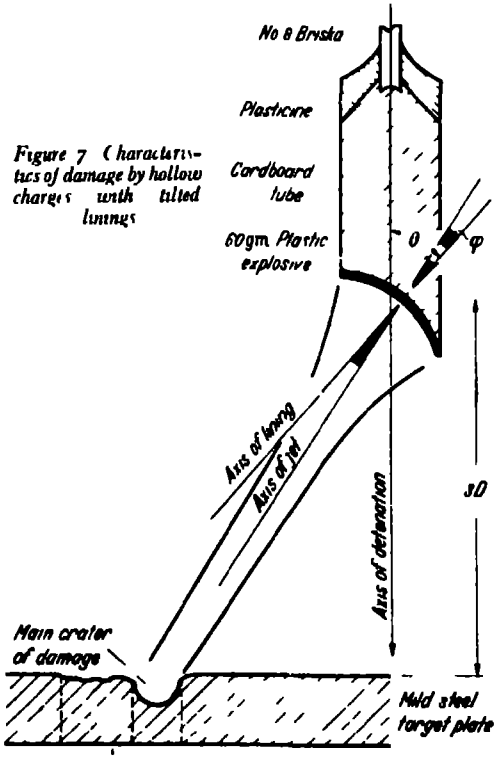

Figure 7 Characteristics of damage by hollow charges with tilted linings

Charges 1 3 in (3 3 cm) from target except *No 1* and *No 15* which were at 0 2 in (0 5 cm) and 0 25 in (0 6 cm) respectively

The percentage erosion is obtained by dividing the loss in weight of the target by the weight of the target metal displaced by the crater

Acknowledgements are due to the late Sir Robert Robertson, K B E, F R S, for his interest and encouragement throughout the course of these investigations and to the Chief Scientist of the Ministry of Supply for permission to publish this account of them The photographs are Crown copyright and are reproduced by permission of the Controller, H M S O

Armaments Research Establishment
Ministry of Supply

(*Received May 1950*)

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Research Correspondence

Estimation of the Surface Areas of Powders from the Temperature Dependence of Adsorption from Solution

Harkins and Gans[1] in 1931 suggested that the surface area of a fine powder might be measured by determining the adsorption isotherm on the powder of a long chain organic compound from solution In the method originally proposed, the amount adsorbed was found by measuring the strength of the solution at equilibrium, by chemical analysis The introduction of the Langmuir trough as a means of analysis for such compounds[2] enables the adsorption isotherms to be obtained more easily, and the method is now simple and convenient

In the literature, adsorption isotherms are usually plotted as the amount adsorbed against the absolute concentration C of the solution However, the maximum range of concentration over which adsorption can be studied is from zero to saturation, and for some purposes it is more useful to use, as abscissa, the relative concentration C/C_0, C_0 being the saturation concentration It is apparent that C/C_0 may be changed in two ways

a by variation of C while keeping the temperature (and hence C_0) constant, and

b by variation of temperature (and therefore C_0) while keeping C constant

If the limiting amount adsorbed does not depend appreciably on temperature, a plot of amount adsorbed against the temperature or its reciprocal (method *b*) should contain a linear portion approximately parallel to the temperature axis, this could then be used to evaluate the surface area

The authors have employed both methods using solutions of stearic acid in benzene The adsorption curves obtained are compared in *Figures 1* and *2* and the surface areas evaluated from them given in *Table I* The good agreement obtained from the two

Table I

Powder	*Area from isotherm* m^2/gm	*Area from temperature dependence* m^2/gm
TiO_2	7 6	7 3
SiO_2	4 6	4 7
TiC	1 23	1 32
SiC	0 54	0 60

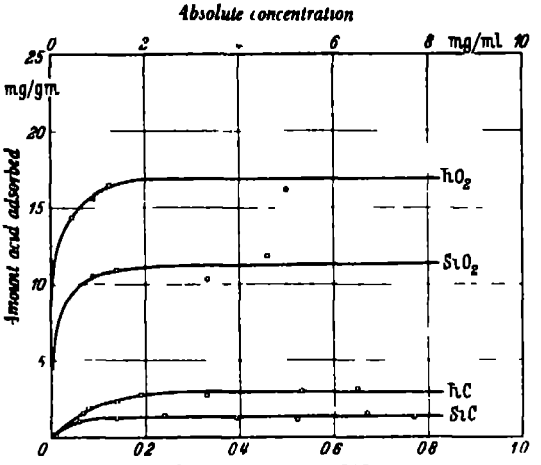

Figure 1 *Adsorption isotherms*

methods will be noted, this confirms the result obtained by HEYNE and POLANYI[3] that the variation with temperature of the limiting amount adsorbed from solution is small

The temperature dependence method possesses two advantages *1* it involves less manipulation, and *2* there is a smaller experimental error

The reason for the second advantage is the following When determining the adsorption isotherm on a particular sample of powder, the solution can be diluted either by adding pure solvent or replacing some of the solution by pure solvent In the first case the volume of solution would increase say tenfold, to cover the necessary concentration range, and with increasing volume of solution a correspondingly larger amount of solute would have to desorb to cause a detectable change in the solution concentration Estimations of the amount adsorbed from concentration determinations would therefore become progressively less accurate with increase in volume If, on the other hand, some of the solution is replaced by pure solvent an error in the estimation of the concentration of the solution withdrawn leads to a corresponding error in the estimation of the solute remaining, this error is cumulative with each replacement In the temperature dependence method these manipulations are not made, only a sufficient volume of solution for analysis need be withdrawn and since this volume may be no more than one half per cent of the total volume of solution the cumulative error is very small

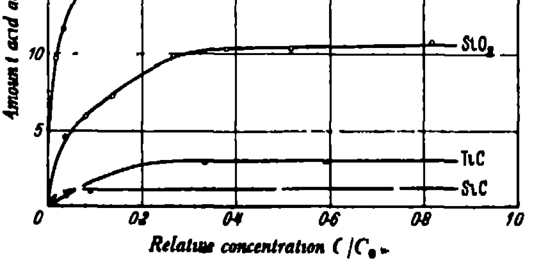

Figure 2 *Temperature dependence of adsorption*

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Iodine Monochloride as an Ionizing Solvent

IODINE monochloride is known to act as a dissociating solvent for potassium and ammonium chlorides[1] and FIALKOV and KAGANSKAYA[2] have shown that the first of these solutes probably forms the ions K^+ and ICl_2^- In the solvent itself the ionic equilibrium $2ICl \rightleftharpoons I^+ + ICl_2^-$ is indicated by conductivity measurements[3], and there is thus an analogy with water and also with non-aqueous solvents like sulphur dioxide[4] and bromine trifluoride[5]

In a further study of solutions in iodine monochloride it has now been found that antimony pentachloride is soluble up to 1 mol per cent, the solution showing an enhanced conductivity which may be explained by the formation of the ionized compound $ISbCl_6$ ($ISbCl_6 \rightarrow I^+ + SbCl_6^-$) When potassium chloride is added to this solution the conductivity is diminished, passing through a minimum when equimolar proportions of antimony pentachloride and potassium chloride are present Further addition of the potassium salt gives a marked increase in conductivity due to the formation of $KICl_2$ The following are conductivity data obtained at 50°C with successive additions of potassium chloride to a solution of 0 0585 mol antimony pentachloride in 1,000 gm of iodine monochloride

Mol KCl/ *1,000gm* ICl	*Molar ratio* KCl/SbCl$_5$	*Sp Cond* (*ohm*$^{-1}$*cm*$^{-1}$ × *10*^{3})
0	—	9 25
0 0157	0 268	9 21
0 0352	0 598	9 15
0 0659	1 121	10 01
0 0880	1 505	11 17
0 1160	1 980	12 94

The occurrence of the reaction

$$I^+[SbCl_6]^- + K^+[ICl_2]^- \rightleftharpoons KSbCl_6 + 2ICl$$

was confirmed by the isolation of potassium hexachloroantimonate in quantitative yield by repeated extraction of the solvent with carbon tetrachloride. This, in terms of the solvent theory of acids and bases[6], is a typical neutralization reaction, the solutes KICl$_2$ and I[SbCl$_6$] reacting respectively as base and acid, in that they give rise in solution to the anion and cation of the solvent. This conception suggests a different interpretation of the results of FIALKOV and KUZMENKO[7], who found that phosphorus tri- and penta-chlorides formed with iodine monochloride the compound PCl$_5$ ICl, which they believed to ionize into [PCl$_4$]$^+$ and [ICl$_2$]$^-$. A solution of the phosphorus compound may, however, be made to react with potassium chloride. The following conductimetric data (50°C) show a more rapid rise on conductivity for molar ratios KCl/PCl$_5$ greater than unity. The initial concentration of the phosphorus compound (PCl$_5$ ICl) was 0 0535 mol per 1,000 gm of ICl

Mol KICl$_2$/ *1,000gm* ICl	*Molar ratio* KICl$_2$/PCl$_5$ ICl	*Sp Cond* (*ohm*$^{-1}$*cm*$^{-1}$ × *10*^{4})
—	—	1 08
0 0121	0 226	1 11
0 0322	0 603	1 15
0 0522	0 977	1 20
0 0872	1 620	1 38
0 1083	2 032	1 53
0 1385	2 575	1 66

It is believed that the reaction is again one of neutralization, expressed by the equation

$$I^+[PCl_6]^- + K^+[ICl_2]^- \rightleftharpoons KPCl_6 + 2ICl$$

though here the product, potassium hexachlorophosphate, was not isolated. In the same way it was possible to prepare potassium hexachlorostannate in iodine monochloride by the interaction of stannic chloride and potassium chloride in a 1 : 2 ratio. The investigation is being extended to include iodine bromide and cyanide as solvents and appears to afford a new approach to the preparation of a number of complex salts

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Synthesis of Organo-silicon Carboxylic Acids

SOMMER, PIETRUSZA and WHITMORE[1] have condensed trichlorosilane with unsaturated hydrocarbons using acetyl peroxide as a catalyst. A similar technique has been used to effect the synthesis of organosilicon carboxylic acids the general reaction being

$$R_3SiH + CH_2{=}CH(CH_2)_xCOOH \rightarrow R_3Si(CH_2)_{x+2}COOH$$

(*I*)

Thus triphenyl silane has been coupled with 9-undecylenic acid to form triphenyl silyl undecylenic acid using benzoyl peroxide as catalyst

Compounds of this type are of interest as possible polar additives for silicone fluids with a view to improving their poor lubricating properties under conditions of boundary lubrication so that wider use may be made of their unique thermal stability and viscosity/temperature characteristics. Preliminary experiments show that, although the solubility of triphenyl silyl undecylenic acid in silicones is low, even solutions of concentrations as low as 0 01 per cent effect an appreciable improvement in the

Table I

Lubricant	*Coefficient of friction*
Silicone Fluid DC 200 *Viscosity = 50 cs at 25°C*	0 24, 0 23, 0 24, 0 245, 0 23 *Mean* 0 237
ditto plus 0 01 per cent *triphenyl silyl undecylenic acid*	0 185, 0 17, 0 18, 0 18, 0 185 *Mean* 0 180

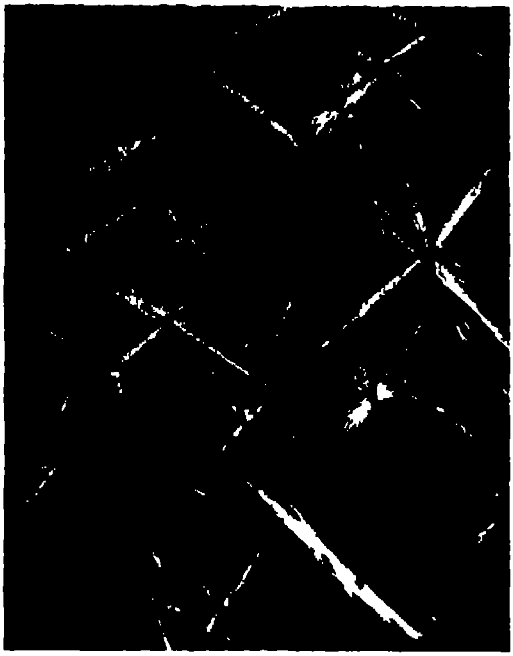

Figure 1 *Crystals of triphenyl silyl undecylenic acid (× 40)*

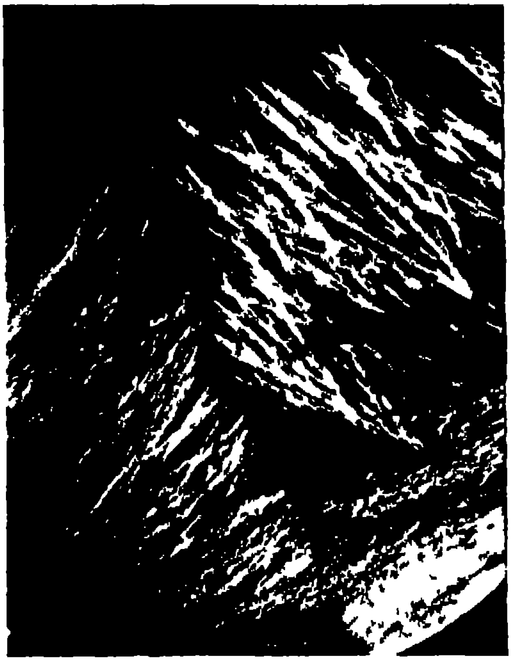

Figure 2 *Crystals of ethyl triphenyl silyl undecylenate (× 40)*

behaviour of these fluids under thin film conditions of lubrication. This is illustrated in *Table I* giving coefficients of friction for brass on brass as measured at room temperature on a friction machine constructed on the lines of that designed by **Chalmers**, **Forrester** and **Phelps**[2].

EXPERIMENTAL

260 gm (1 mol) triphenyl silane[3], 30 gm (0.16 mol) 9-undecylenic acid and 3.15 gm (0.013 mol) benzoyl peroxide were dissolved in 250 ml hexane. The apparatus was swept with nitrogen and the reaction mixture refluxed on a waterbath maintained at 75°C for 14 hr in a continuous stream of nitrogen. (Half life of benzoyl peroxide at 70°C being *c* 13 hr.) After recovery of hexane and excess triphenyl silane the viscous residue was fractionated in a Hickman molecular still to yield 70.8 gm (96 per cent theoretical) of triphenyl silyl undecylenic acid *I* distilling at 250 to 270°C at 7×10^{-3} mm. *I* is soluble in a wide range of organic solvents and was recrystallized from benzene to give needles (*Figure 1*), m.pt. 58.5 to 59°C. Negative reaction with iodine in benzene solution confirmed that condensation had taken place at the ω-position.

[Found[4] C 78.22, H 7.91, Si 6.4, Eq. wt. 450
$C_{29}H_{36}SiO_2$ requires C 78.5, H 8.1, Si 6.3, Eq. wt. 444]

The ethyl ester of *I* was prepared by conventional esterification and also by condensation of triphenyl silane with ethyl undecylenate. Purification by molecular distillation (255 to 280°C at 7×10^{-3} mm) and recrystallization from benzene gave needles (*Figure 2*) of ethyl triphenyl silyl undecylenate m.pt. 49°C.

[Found[4] C 78.6, H 8.4, Si 5.97
$C_{31}H_{40}SiO_2$ requires C 78.8, H 8.47, Si 5.93]

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Photoelectric Methods for Metal Optics

Photoelectric and electronic techniques have been widely used in spectroscopy but little use has been made of them in polarimetric work. This preliminary note gives details of these methods used to study metal films and surfaces.

a **Kent** and **Lawson**'s method of detecting circularly polarized light[1] may be used for determination of principal incidence and azimuth. Light reflected from the metal passes through an analyser rotating about 45 r p s and falls on a photocell feeding a tuned amplifier the output being observed on a cathode ray oscilloscope (C R O)

b A double-image prism may be used with a modulated light source (*Figure 1*) The orientation of the vibration ellipse is determined by setting the double-image prism mounting in the four positions of zero output from the bridge The axial ratio is found electrically by adjusting the bridge for zero output when the axes of the prism and ellipse coincide

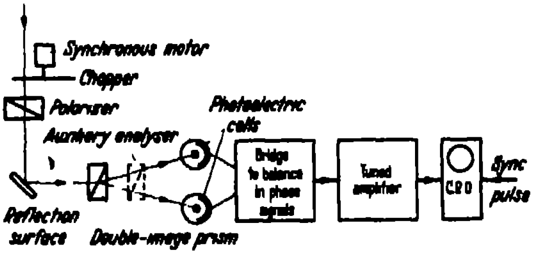

Figure 1 Photoelectric method using modulated light source

c A double-image prism used with a rotating analyser (*Figure 2*) enables the orientation and axial ratio to be determined by a single setting, since the bridge must be balanced for both amplitude and phase, and the selected modulation components are in antiphase only when the axes of the double-image prism and ellipse coincide

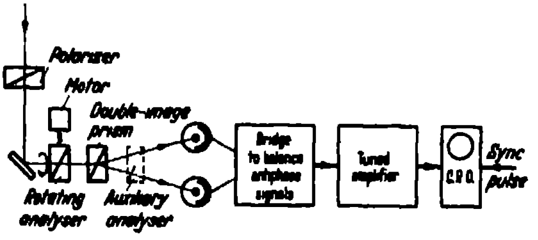

Figure 2 Photoelectric method using rotating analyser

d The signals in methods *b* and *c* may be balanced by optical rather than electrical means by using an auxiliary analyser placed after the double-image prism, which should preferably be, in this case, of Wollaston rather than Rochon type[2]

In metal optics Δ, the relative phase change, and $\varrho = \tan \psi$, the ratio of the Fresnel reflection coefficients, are usually required[3] In methods *b* and *c* these quantities must be deduced from the measurements, but they may be obtained directly[4] if the axes of the reflected ellipse are arranged to be at 45° to the plane of incidence

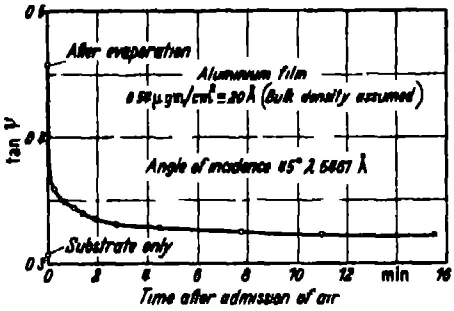

Figure 3 Variation of tan ψ with time for aluminium film

Other workers have used visual[5] or photographic[6] methods similar in principle, but the photoelectric methods described have a number of advantages They are rapid, accurate, and applicable over a wide wavelength range without recalibration as optical compensators are eliminated The best theoretical accuracy in measurement of Δ and ψ is about 1 minute of arc Our experience suggests that modulation at the light source is preferable since a rotating analyser increases both experimental difficulties and possible sources of error

As an example of results which can be obtained with our methods the variation of tan ψ with time for an aluminium film is shown in *Figure 3* At $t = 0$, shortly after evaporation of the film, air at atmospheric pressure was introduced into the vacuum chamber The weight of the film was found by a vacuum microbalance made in this laboratory by A W Crook

Thanks are due to the Royal Society and the Carnegie Trust for grants for apparatus and to the Ministry of Education for grants for two of us (J F A and P L C)

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Commentary: Japanese Science and Technology

THE RECENT EMPHASIS on industrialization of countries in Asia and the Far East draws attention to Japan's potential role in the introduction of technology to her neighbouring nations The Orient is industrially the most undeveloped region in the world and it is recognized that great transformations could come about with present available technology Although Japan has been open to western technology for only about eighty years, she has effectively learned to adapt this technology to her local problems and so could act as an intermediary in the industrialization of other eastern nations

Because of her short period of contact with western technology and her isolation prior to and during the 1939–45 war, Japan is roughly 15 years behind England and the U S A Exceptions to this are the applied fields indigenous to Japan such as sericulture, agriculture and fisheries where the Japanese show outstanding skill, not only in practical methods but also in the application of recent scientific research In some subdivisions of these fields Japan may possibly lead the world

In the fundamental sciences Japan has learned to appreciate and contribute to the advancement of knowledge She has made major contributions to mathematics, physics, biology and chemistry Throughout 1939–45 she was able to keep abreast of the field in theoretical nuclear physics Last year Hideki Yukawa was awarded the Nobel Laureate for his contributions to the meson theory Because of the social structure in Japan and because of the very limited amount of equipment her contributions have been restricted, except in a few instances, to the theoretical sciences

Curiously, this creative ability of the Japanese has seldom been applied to industry Industrial technology appears to have been directly imported from the West whereas her fundamental science is deep rooted Following the argument that the slave system in ancient Greece prevented an industrial revolution when such brilliant scientific advances as Euclid's geometry were being made, it can be reasoned that the feudal system in Japan discouraged the native development of that technology which had to be imported The advances Japan made in sericulture, agriculture and fisheries were primarily made by her intelligent and industrious farmers and fishermen She has had numerous brilliant scholars in the theoretical sciences, but these talents even today are rarely applied to practical problems

Since the cessation of hostilities several noteworthy attempts to overcome the gap between fundamental science and industry have been made in Japan. The new Science Council of Japan and a governmental Scientific and Technical Administration Commission have been formed These will be described later. Private industrial laboratories such as the Scientific Research Institute have been organized. This Institute, formerly the non-profit organization called the Institute of Physical and Chemical Research (Riken), received support from private and governmental appropriations. The new Institute is now a private corporation dependent solely on profit from its technical developments It has some of the outstanding scientists in Japan on its staff headed by Yoshio Nishina, an internationally known physicist If the gap is to be filled, it will be done by such organizations as the new Institute and a really effective coordination between the laboratories of the larger industries and their production plants

England and Germany have had the greatest pre-war influence on Japanese science Germany's influence is particularly prominent in medicinal fields Available evidence indicates that Germany made no significant scientific contributions to Japan during the war A good illustration both of England's pre-war influence and effects of this influence can be given by an account of J A Ewing's visit to Japan Ewing was a young man during his stay in Japan and worked with the Japanese on his early researches in magnetism The Japanese rightly trace their success in one of the few isolated cases of applied sciences to the inspiration left from Ewing's visit Kotaro Honda, one of the men influenced, received prizes from the Royal Society and the Faraday Society, and has had his commercial methods of producing magnetic metals adopted in western nations

Encouraged by the initial success in carrying out research with the limited facilities available in Japan and recognizing the need for trained Japanese personnel to build their railways, steamships and telegraph systems, Japan began negotiations to start a college of engineering The first intensive construction of communication systems was started by foreigners after ratification of the first treaty with Europe and America Negotiations for training technical men were initiated by requesting the Export-Import firms in Yokohama to import good teachers An order was communicated to the Jardine-Matheson Co who requested aid from Sir William Thomson, well known to the company for his success in laying the Atlantic cable Highly interested in the subject, Thomson promised to send some of the best graduates of the University of Glasgow to Japan Among the early teachers were Dyer (mechanical engineering), Divers (chemistry), Milne (mining), Ayrton (electricity), Alexander (civil engineering), Gray (telegraphy) and Perry (mathematics) These men formed the nucleus of the first college of engineering in Japan, which was called the Kobu-Daigaku

Japan has a population of 80 million people increasing at about one million per year in an area about that of California—a country that at present can raise only about 80 per cent of its food requirements She has very limited natural resources and at present finds foreign trade oppositions partly due to her actions during the war

To meet this grave economic problem Japan has the assets of an industrious people, competent scientists and ability to adapt western technology to her indigenous needs She hopes to use this imported technology and her native scientific talent to conserve her limited resources by improving her manufacturing industries which serve the export trade and through the sales of services of her technicians to neighbouring nations interested in industrialization

The nations of the Orient are likely to follow Japan's industrial history by first developing agriculture, fisheries, ceramics and textile industries Japan with her shortage of raw materials is eager to exchange technical knowledge and manufactured goods for food and raw materials from her neighbours She can export irrigation, fertilizer, transportation and communication equipment necessary for industrialization

SCIENCE DURING THE OCCUPATION

The occupation of Japan is controlled by the Supreme Commander of Allied Powers (SCAP) Part of SCAP's function is to implement the directives of the Far East Commission regarding science and technology After a thorough survey of Japan's scientific potential, it was found that Japan had contributed little scientifically towards the war effort. Some of her scientists had ideas for developing such things as homing bombs and proximity fuses but these never got beyond an elementary laboratory stage

Japan is still prohibited from construction of civilian or commercial aircraft, mass separation of isotopes and any research activity directed towards warlike ends. The limitations on research were based on the Potsdam recommendations and the Far Eastern Commission directives. The Japanese were informed that research and teaching for the extension of scientific knowledge would be permitted except where directed towards warlike activities. Economic limitations proved to be the real restriction on research. Rather than emphasize restrictions, the occupation encouraged the scientists of Japan to tackle the immediate and pressing problems associated with food, clothing, housing, health and export.

There are no limitations on theoretical research in any field and there are no restrictions on publication of research results, whether current or on research performed during the war. Japanese scientific organizations were encouraged to resume their normal peacetime associations with international bodies of science by ensuring that at least some dollar and sterling funds were available for this purpose.

The international mails are now open for the exchange of scientific and technical periodicals, books or manuscripts. Japanese technologists are permitted to accept invitations from foreign institutions but in general, because of the pound-dollar shortage,[1] expenses usually have to be supplied by the foreign institution. The percentage of the national budget for science and technology was raised from 0.3 to 0.75 per cent with emphasis on those projects which could aid economic recovery.

Compared with the rest of Japan, the laboratories survived the bombings fairly well. Most damage was inflicted on industrial laboratories although a few universities also suffered severely. The laboratories at the University of Literature and Science in Hiroshima and Nagoya Imperial University were probably the most severely damaged. The universities at Osaka and Sendai, Waseda and Keio in Tokyo sustained some damage to their laboratories but many others such as the Imperial Universities of Tokyo, Kyoto, Kyushu and Hokkaido suffered no destruction.

The invading troops damaged some scientific apparatus, but considering the circumstances the damage was not great. Most publicity has been given to the destruction of four cyclotrons in Japan but this destruction probably worked in the best interests of Japanese science for it drew attention to the problem of the place of science in society and the necessity for adopting a reasonable attitude.

REORGANIZATION OF THE NATIONAL BODIES OF SCIENCE

The fundamental policy adopted by the occupation in regard to the reorganization of the national scientific bodies was that any reformation which was to be permanent had to be initiated and implemented by the Japanese themselves. Occupation officials worked closely and co-equally with the Japanese scientists in the problems of reorganization and two groups from the United States National Academy of Sciences were sent to Japan to discuss problems associated with scientific organizations.

There were three important national scientific organizations in Japan in 1945—The Imperial Academy, The National Research Council and The Japan Society for Promotion of Science. The first two were governmental organizations and the last was private but received most of its money from the government. The functions of the three organs were overlapping in some respects and the younger scientists in Japan considered that the old organs were not representative and not effective in overcoming the difficulties in Japan both during 1939–45 and after. The more active scientists requested that they be given an opportunity of presenting plans for more effective and representative organizations. As a result of a long study by the Japanese and action by the Japanese Diet, the National Research Council was abolished and a new Japan Science Council (JSC) was formed on 20 January 1949. The Council was chosen by election. The voters were the qualified scientists of Japan who numbered in the first election some 40,000. The present top officers of the Council are Naota Kamayama, Dean of Engineering at Tokyo National University, President, Yoshio Nishina, President of the Scientific Research Institute Ltd, Vice-President of Natural Sciences, and Sakae Wagatsuma, Professor of Law at Tokyo National University, Vice-President for the Social Sciences and Humanities. Election of officers and members is to be held every three years. The Council consists of the following 7 divisions

1 Literature, Philosophy and History
2 Law and Politics
3 Economics and Commerce
4 Natural Sciences
5 Engineering
6 Agriculture
7 Medical Sciences, including Dentistry and Pharmacy

Each division has 30 members who represent various subdivisions and seven geographical districts of Japan

It will be noted that the word 'science' as used for organizational purposes in Japan includes all fields of higher learning The functions of the Science Council of Japan are given in the preamble of *Law No 121, 1948*, which follows

'The Science Council of Japan shall hereby be established, on the conviction that science provides the basis of a cultural country and with a view to fulfilling its mission of contributing by the joint will of the scientists throughout Japan to the peaceful rehabilitation of this country and promotion of the welfare of human society as well as to the advancement of science of the world, in cooperative relations with academic societies of foreign countries'

The Council can be called upon by the government for advice on such matters as

1 distribution of government grants and subsidies for the promotion of scientific research
2 administration and budgets of governmental institutions and laboratories
3 guidance in researches, and the training of scientists in universities and their attached institutes

JSC is now a member of the International Council of Scientific Unions National Committees have been formed for the research liaison of some twenty branches of science, including physics, chemistry, astronomy, botany and zoology, and some of these are members of International Unions

On 20 January 1949 the Japan Imperial Academy became the Japan Academy of Science as an honorary organ of the Science Council for awarding prizes for outstanding research and in recognition of other outstanding scientific performances New members of the Academy are decided upon by a joint committee of JSC and the Academy

In addition, in order that the government could coordinate its scientific and technical interests in the various Ministries and to maintain close contact between governmental agencies and JSC, a governmental body called the Scientific and Technical Administration Commission (STAC) was also formed on 20 January 1949 There are at present 20 members of this Commission, half of whom represent JSC, the remainder being Vice-Ministers of the Cabinet The Prime Minister is the Chairman of STAC Article 2 of *Law No 253, 1948* which set up STAC states

'The Commission shall deliberate and make recommendations on the following matters *1* measures necessary for reflecting the reports or recommendations made by JSC to administrative bodies, *2* selection of matters which are to be referred to JSC for consultation by the government, *3* method of execution of international enterprise concerning science and technology which should be carried out by the government, *4* liaison and coordination of matters relative to science and technology which are under the jurisdiction of the government administrative agencies'

The application of scientific talent to the development of indigenous industries as well as the encouragement of basic research was planned by the new organizations However, because of economic limitations imposed partly by difficulties of reparations and decontrol of the Zaibatsu companies, private industry has not yet been effective in this cooperation

As a result, approximately 80 per cent of research is presently supported by the government and a good share of this by the Ministry of Education Now that decisions regarding reparations and cartels have been made private industry is seeking aid to meet the highly competitive market it faces

The explosion at Hiroshima dramatically demonstrated the status to which all branches of science had grown The people of the eastern nations have also appreciated that the sociological and economic implications resulting from science, the growth of which may not previously have been recognized by the layman, demanded recognition The intelligent peoples of the East who live in the most undeveloped areas of the world recognize that their countries must undergo the greatest transformations Although Japan is far behind the West in applied technology, she has learned how to apply this technology to the local problems of the East and could aid her neighbours in these transformations. A continuing study of the effects of this industrialization should be made in order that both East and West can govern their activities to use technology for better understanding and cooperation

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Measurements in the Upper Air by Radio Sonde

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PHYSICAL studies in the upper atmosphere are attracting much attention at the present day, partly as an aid to meteorology and partly for more fundamental investigations such as cosmic radiation. Meteorology requires not only routine measurements of pressure, temperature and humidity in three dimensions for use in forecasting, but also research in such subjects as radiation balance, chemical constitution (including determinations of water vapour and ozone concentrations), electric field and conductivity measurements, wind turbulence *etc.*

Much work in all these directions can be carried out from aircraft, but the comparatively low ceiling (12 km) of all normal aircraft, corresponding to a pressure of 200 mb, is insufficient for many purposes. Apart from the use of rockets, which are still in a very early stage of development, the only method of reaching greater heights is by means of balloons which allow attainment of altitudes of 30 to 35 km, corresponding to air pressures of 5 to 10 mb.

The apparatus attached to the balloon may be of two types, automatic recording instruments or radio sondes. The former require to be recovered after their descent, but radio sondes transmit immediately the results of their measurements to a ground station. Recording instruments are quite useless for routine meteorological forecasting owing to the uncertainty and delay in obtaining the record. In other fields of research they are often used providing that the probability of recovery is good, a condition which is not fulfilled in maritime areas such as the British Isles, nor in sparsely populated countries. But even when it is safe to use them, it is found that recording instruments often demand heavier and more complicated equipment than do radio sondes, and only in a few types of measurement, such as analyses of the chemical constitution of air or spectroscopic work, is the radio sonde technique unsuitable.

Any radio sonde can be considered as consisting of three parts: *1* the sensitive element which responds to the change in the variable which it is required to measure, for instance air pressure or the vertical flux of cosmic ray mesons; *2* a means of expressing the indications of the sensitive element as an electric signal which modulates *3* the radio transmitter. In general at least two physical quantities must be measured, of which one, air pressure, is treated as the independent variable. Where the actual geometric height is required, this can be computed when the temperature dependence on height is also known.

A requirement common to radio sondes of all types is extreme lightness. The load capacity of a balloon depends inversely on the height which it is required to reach. In routine meteorology altitudes of 20 km are desirable and in most research problems, particularly those connected with cosmic radiation, the maximum height obtainable of 30 to 35 km is frequently insufficient. This maximum height, at which the balloon bursts, is set by the rapid deterioration of rubber in the upper atmosphere, due probably to the combined influence of extreme cold, ultraviolet radiation and ozone. A common size of balloon weighs 700 gm and when inflated on the ground to a diameter of 1.8 m can carry about 1.5 kg to 20 km on a useful proportion of occasions.

CLASSIFICATION OF RADIO SONDE TYPES

There is a clear-cut distinction in the design of instruments used for routine meteorological observations from those required for research purposes, a distinction which arises from the numbers used. Consumption of meteorological radio sondes in Great Britain and colonial possessions is at the rate of tens of thousands per year. Cost is therefore an important consideration, which implies a simple design suitable for mass production. In research problems the instruments will usually be made individually and by hand. For this reason it is convenient to divide radio sondes into two broad classes, standard instruments for general use and those for special purposes.

Instruments for routine meteorological use— These must measure pressure, temperature and relative humidity. The sensitive elements are: for pressure, usually an evacuated 'aneroid' capsule, and for temperature, generally a bimetallic strip. No really satisfactory way of measuring humidity is available. The change in length of a hair or strip of gold beaters' skin is commonly used, but the change in resistance of a hygroscopic film on the surface of an insulator is employed in the American radio sonde.

The methods of translating the indications of the sensitive elements into electrical signals are very diverse, but they may be arranged in the following scheme which covers all instruments in large scale use:

a variation of radio carrier frequency

b variation of an audio modulation frequency

c chronometric coding

d Morse coding

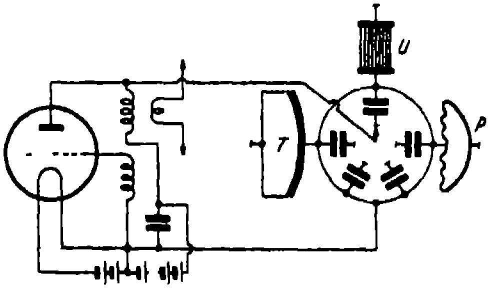

Figure 1 The Väisälä radio sonde P Aneroid capsule, T Bimetallic strip, U Bundle of hairs

Variable carrier frequency— In this system, the transmitter radiates a continuous wave at a frequency which varies with the parameter (pressure, temperature, or humidity) which it is desired to measure The most successful example of this type is the Finnish radio sonde, designed by V VAISALA[1], shown diagrammatically in *Figure 1* Each meteorological element is attached to one plate of a parallel plate air dielectric condenser, the capacity of which is therefore caused to vary as a function of pressure, temperature or humidity Each condenser is connected in turn through a switch to the resonant circuit of the radio frequency oscillator and controls its wavelength However, such an oscillator is not remarkable for its stability, so that frequency will vary also with the voltage of the power supply and with the temperature of the inductance To correct for these changes, two fixed ceramic condensers are also included in the switching cycle Their capacities are adjusted to approximately the upper and lower limits of those of the variable condensers Measurement of three frequencies, when the two fixed and one variable condenser are successively in circuit, enables the operator to eliminate to a first approximation the stray capacity and inductance of the oscillating circuit and to derive the capacity of the variable condenser which, on reference to a calibration curve, gives the value of the associated meteorological quantity

The switch is driven by a wind vane, similar to a cup anemometer, which rotates in the air stream created by the ascent of the balloon It turns approximately twice per second, so [illegible] each second there are ten bursts of oscillation The operator on the ground tunes in to each frequency as he requires and when in tune depresses a key which prints on a moving paper band a record of the frequency A special scale is used for subsequent measurement of the record and automatically makes the required reduction of the readings

The Väisälä radio sonde is remarkable for its small size and extreme lightness It measures 5 cm × 9 cm × 10 cm, and weighs 365 gm complete with battery No other radio sonde, with the exception of a Japanese type of crude design, approaches it in size or weight At the same time it compares favourably in accuracy with other types, although figures for the accuracy of radio sondes actually in use are hard to procure owing to the lack of any standard for comparison

A grave disadvantage in the use of all variable radio frequency sondes is the large band width required The Väisälä instrument for instance radiates over a band about 3 Mc/s broad centred on 25 Mc/s The internationally agreed band for meteorological purposes in Europe is only 0 5 Mc/s broad in this region While the low power of a radio sonde occasions little interference to other stations the converse is not true, and in districts where the radio traffic is heavy it is necessary to keep within the accepted meteorological band, which is reasonably free from outside interference

Variable modulation frequency— In this class the transmitter operates at a fixed frequency, which is modulated by an audio frequency varying with the meteorological quantities to be measured This modulation tone is measured on the ground Two widely used radio sondes belong to this class, the British Meteorological Office type and that used in the U S A

The British instrument was developed during the war and has been described by E G DYMOND[2] It is shown diagrammatically in *Figure 2* In the tuned circuit of a modulating oscillator are placed variable inductors These inductors have mumetal cores, in the magnetic circuit of which are air gaps the widths of which are controlled by the meteorological elements A movement of 3 mm causes a change in frequency from 700 to 1,000 c/s By careful design of

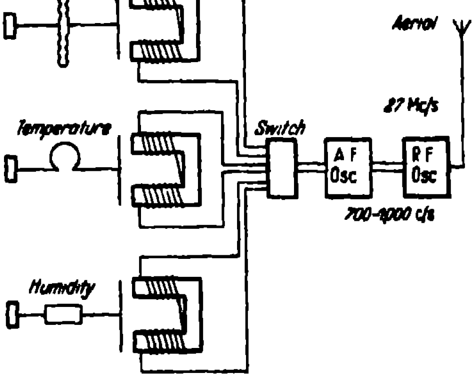

Figure 2 Schematic diagram of the British radio sonde

the oscillator, frequency is made sensibly independent of battery voltage The three inductors, for pressure, temperature and humidity, are connected in turn to the oscillator by a wind driven switch, as in the Väisälä radio sonde This however turns more slowly so that transmission of each signal takes place for 6 sec The weight of the instrument with batteries is 1 4 kg

The ground equipment consists of a normal communications receiver, the output signal of which is applied to the vertical plates of a cathode ray oscillograph A calibrated variable oscillator of high precision feeds on to the horizontal plates The frequency of this oscillator is controlled manually to obtain a stationary Lissajou figure on the screen, which occurs when the frequencies of the incoming signal and of the ground oscillator are equal

In the American instrument, developed by H DIAMOND, W S HINMAN, F W DUNMORE and E G LAPHAM[8], the modulation frequency is controlled by a change in resistance The temperature element is a short thin rod of an electric semi-conductor with a very high negative temperature coefficient of resistance, and the humidity element employs the varying resistance of a hygroscopic film on an insulator Each resistor is connected in turn through a switch to the grid circuit of a blocking oscillator, which modulates the radio oscillator with a pulse frequency ranging from 10 to 200 c/s As blocking oscillators are inherently unstable in frequency, two fixed resistors can also be switched in to provide standards of reference

The switching operation is performed by the pressure element itself, a large aneroid capsule which moves an arm over a bank of 75 contacts It will be seen from *Figure 3* that when the pressure pointer is over an insulating segment the relay is not energized and the temperature resistor is connected to the network controlling the frequency of the blocking oscillator Four out of every five contacts are connected in parallel to the relay, which when energized transfers the humidity resistor into the network The remaining contacts (called high and low reference contacts) add the fixed resistors to the circuit for standardization purposes Each switching operation occurs at a definite pressure, determined through the initial calibration The fact that pressure measurements can only be made discontinuously at 75 predetermined points is of little disadvantage, as in practice pressure changes smoothly and in one direction with time

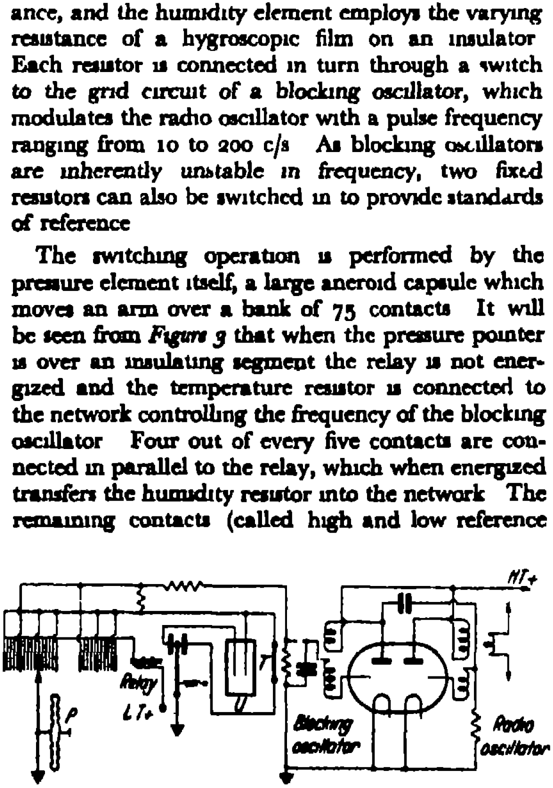

Figure 3 The Diamond-Hinman radio sonde P Pressure unit, T Thermometric resistor, U Humidity resistor

The ground equipment embodies automatic recording, in which the audio frequency signal passes to a frequency measuring circuit from which the output feeds a pen recorder

The British and American radio sondes worked at times side by side during the war so that some comparison of their performances was possible While it appeared that the British instrument had some advantage not only in accuracy but also in reliability, it should be noted that both types have been in a state of continual modification in detail, so that no up to date comparison is possible

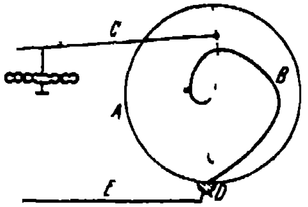

Figure 4 Canadian chronometric radio sonde

Chronometric coding— This principle was first put forward by H OLLAND in the last century, as a means of transmitting instrumental readings over a telegraph line It admits of many variations in arrangement, and the one employed in the Canadian radio sonde will be described A disk *A* (*Figure 4*) is maintained in uniform slow rotation by an electric motor It carries on its surface a raised scroll *B*, in the form of an equiangular spiral A movable arm *C*, attached for example to a pressure element, makes contact at its free end with the spiral once during every rotation of the disk Another fixed arm *E* also makes contact with the disk at *D* once per revolution It is evident that if the disk is turning steadily the time between the reference contact *D–E* and varying contact *B–C* will change as *C* moves to engage different portions of the spiral, and it will therefore be a function of the pressure to be measured The contacts are in the high tension circuit of the transmitting valve which therefore sends out pairs of pulses, the spacing of which in time gives the required information at the ground Further contact arms coupled to a coiled bimetallic cylinder and to a strip of gold beaters' skin provide two additional pulses giving temperature and humidity The disk rotates at 4 r p m and is driven by a simple motor fitted with speed control

On the ground the radio signal is passed after detection to a recorder A broad band of paper is fed forwards at a constant slow rate under a pen which marks it with a dot whenever a signal comes through The pen is traversed across the paper mechanically, in a direction perpendicular to its direction of travel, at such a rate that one traverse corresponds to one rotation of the radio sonde scanning disk The pulses due to the fixed reference contact will therefore make on the paper a line of dots, parallel to the direction of motion of the paper The pressure, temperature and humidity pulses make oblique lines, showing the variation of these quantities with time The speed of traverse can be controlled manually to keep the reference line in its proper position

The accuracy of this form of radio sonde depends primarily on speed constancy of the driving motor Slow changes are not important as they can be allowed for in the manual control of the recorder, but changes within one period of rotation of the scanning disk cannot be compensated Speed constancy can best be attained by driving the disk by clockwork, as was done in the Lang radio sonde used by the German civilian weather service before 1939 With this arrangement, however, the disk moves in jerks, and the ‘ resolving power ’ is limited by the duration of one tick of the clock Clockwork with its discontinuous motion does not provide an ideal form of motive power

Another line of approach to improve the potential accuracy of the chronometric radio sonde is that adopted in the pre-war French instrument due to M Bureau In this the scanning mechanism is driven by a governor controlled spring motor, but the working is made independent of the speed by radiating along with the usual signal a series of pulses derived from a contactor driven from the gearing These pulses are suppressed during the period of contact of one of the arms C (*Figure 4*) or of the fixed contact with the rotating member so that the angular motion of the scanning disk can be measured as a function not of time but of the number of pulses between contacts The fact that the Bureau radio sonde was of rather poor precision was due not to the principle of operation but to faults in mechanical design It was however one of the first successful instruments, and in its day did much useful work A simpler modified form has been developed and is now in use in India

While the Bureau system is theoretically capable of high precision, it is found to make great demands on instrument making technique The Canadian radio sonde, with its extreme simplicity and accuracy of about 1 per cent, still remains the only chronometric radio sonde in large scale use It seems that higher precision cannot be attained except in individually constructed apparatus adapted for limited research use but not for routine investigations

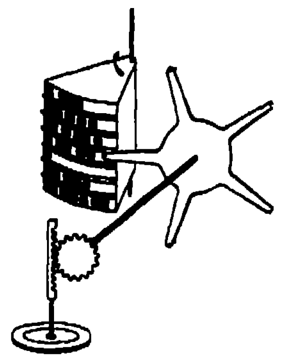

Figure 5 Morse coding unit, for simplicity only 7 letters are shown on the rotating sector. it should carry the whole alphabet

Morse coding — In radio sondes of this category no attempt is made to transmit a continuous function of pressure, temperature or humidity, but the range of variation is split into short sections of say 5 mb each and a Morse character is allotted to each section In order to handle the total range of some 1,000 mb, the alphabet must be repeated at appropriate intervals One of the earliest radio sondes, due to G Moltchanoff, utilizes this principle and was in regular use in Russia up to and during the war The system was also used extensively in Germany, partly for balloon borne radio sondes but more generally for automatic weather stations installed by submarine on floating buoys in the ocean or on isolated uninhabited islands

The German mechanism for deriving the Morse characters is shown in *Figure 5* An insulated contactor segment is rotated by electric motor at about 2 r p m and carries in channels on its surface a series of metal segments corresponding to Morse characters A star shaped wheel, rotated by the meteorological element makes contact with these segments during their rotation, completing the high tension circuit of the radio transmitter Three such star wheels, one for each meteorological variable, can be disposed round the axis of the contactor sector so that in each revolution three letters are transmitted corresponding to pressure, temperature and humidity The accuracy is necessarily limited to the finite range corresponding to movement of the star from one channel to the next, but good mechanical design makes the arrangement very reliable

In all other types of radio sonde an integral part of the apparatus is the receiving mechanism, which can contribute its own errors, but here no special receiving gear is required as any W/T operator can take down the signals by ear, a matter of great convenience especially in war time Ideally this system is unsatisfactory because it should be a cardinal principle in the design of all balloon borne instruments that if any complicated mechanism or circuitry is required, it should be placed on the ground where it can be inspected and adequately maintained rather than in the air borne unit where any failure is impossible to correct and generally difficult to diagnose.

TRANSMITTER AND BATTERIES

Features common to all radio sondes are the transmitter proper and the batteries. As a typical example of radio oscillator the British instrument may be mentioned; it uses a normal battery triode in a Hartley circuit oscillating at 27.5 Mc/s. A radio frequency output of about 40 mw is led to a half-wave end fed aerial which also acts as support for the instrument. This power is sufficient for efficient reception at a range of 160 km when the transmitter is at an altitude of 20 km, and it appears that the limit in range is in fact set by the distance of the optical horizon. Radio sondes have been heard at distances of over 300 km. Higher frequencies are necessary on the American continent as the 27.5 to 28.0 Mc/s band is not available, and at present 400 Mc/s is employed.

The battery is a most important component as it contributes the largest single item of weight. Dry batteries are still used in some instruments. They have been extensively developed in recent years but, in spite of their great convenience, they remain relatively heavy and their shelf life before use is limited, a factor of importance when radio sondes are used in out of the way locations as in tropical or polar regions. V. VÄISÄLÄ modified the conventional lead-acid battery by replacing the negative with a zinc plate which not only reduced weight but increased the E.M.F. per cell from 2.0 to 2.4 v. The battery is only required to operate for from one to two hours, and this very heavy discharge rate allows the plate thickness to be reduced to the minimum for mechanical strength. The latest British batteries, developed from those of Väisälä, consist of high tension units with positive plates measuring 24 mm × 10 mm × 1.2 mm, assembled in moulded cases in blocks of 28 cells. They will deliver 30 ma for 1.5 hours or 10 ma for 5 to 6 hours. At the latter rating they weight 45 gm per watt-hour capacity when filled with acid. Low tension cells are even more efficient, weighing 27 gm per watt-hour. As these batteries are stored in a dry state their shelf life is long. No perceptible deterioration is detectable after 12 months of storage. They are made active by adding sulphuric acid, and are ready for use about an hour after filling.

INSTRUMENTS FOR RESEARCH

No general classification of radio sondes is possible under this heading, as each problem demands its own design. However, a few types will be discussed.

Cosmic radiation—This subject has occasioned the greatest activity. In general, measurements may be made either with an ionization chamber or with Geiger-Müller counters. Ionization chambers do not lend themselves readily to radio sonde techniques but mention should be made of an apparatus described by R. L. DOAN[4] and C. D. KERN[5]. In this the ionization current was measured by the rate of charging of an electrometer. A beam of light reflected from the electrometer mirror falls at full scale deflection on a photocell, the output of which is used to earth the moving system and to send out a radio signal. The interval between signals is therefore an inverse measure of the current. The apparatus is, however, elaborate and heavy (19 kg) and does not appear to have met with much success.

Geiger-Muller counters on the other hand are admirably suited for this type of work as the pulses from them can be readily applied to modulate the transmitter. Combination of counters in coincidence or anticoincidence presents no difficulties and scaling circuits can also be incorporated, although the principle of keeping the air borne equipment as simple as possible suggests that it is better to have the scaling circuits on the ground.

The high tension supply of 1.0 to 1.5 kv for the counters presents one of the principle difficulties. In early work batteries were used, adding much weight to the load. By mechanical switching, a bank of condensers may be charged in parallel from the transmitter high tension supply, and discharged in series through the counters. A more reliable and simpler method is to generate the voltage electronically[6]. Whatever the method used the greatest care is necessary to prevent corona discharge, as at the greatest heights the breakdown voltage of air will be little above that required to operate the counters.

Temperature control of the apparatus is frequently desirable especially if self-quenching counters filled with alcohol are used, as these begin to behave anomalously when cooled below 5°C. The method first introduced by E. REGENER is generally used. The whole apparatus is enclosed in a 'gondola', usually a light aluminium framework and covered with a double envelope of cellophane. This gondola constitutes an efficient greenhouse, in which the apparatus within absorbs solar radiation, the energy of which is trapped by the cellophane. Temperature control can be achieved empirically by balancing absorbing against reflecting surfaces. It should be noted that the danger with this type of control is from excessive heating rather than cooling of the apparatus. In the author's experience temperatures of + 50°C or more may be obtained when the external air temperature is − 65°C. With correct proportioning, however, it is possible to maintain the internal temperature within a range of 10C° during the flight The control of course fails at night, when apparatus sensitive to low temperatures cannot be used

The weight of cosmic radiation and other research apparatus is generally far greater than that of meteorological radio sondes By using a number of large balloons arranged on a long string, weights up to 6 kg can be lifted to 30 km on a useful number of occasions Equipments weighing up to 30 kg have been designed but great heights have not been obtained with them, nor are they likely to be achieved with existing balloon technique

OTHER APPLICATIONS OF RADIO SONDE TECHNIQUES

The ultraviolet intensity of the sun has been measured as a function of height[7], using a cadmium photocell placed in the grid circuit of a blocking oscillator The current through the cell controls the grid potential of the valve and hence the pulse repetition frequency The blocking oscillator forms part of the normal Diamond-Hinman radio sonde, with pressure element but without temperature or humidity resistors A series of filters could be rotated before the photocell by an electric motor, so that the intensities of several narrow bands of the solar spectrum could be investigated By this means W W Coblentz and R Stair[7] determined the distribution of ozone in the atmosphere, because absorption by ozone is responsible for the limit in the spectrum in the neighbourhood of 3,000 Å

Another adaptation of the Diamond-Hinman radio sonde is due to K Kreielsheimer and R. Belin[8], who measured the vertical electric potential gradient in the atmosphere A vertical wire 20 m long is found to develop a corona discharge at the ends when the field exceeds 3 v/cm, the intensity of the discharge increasing with the field above that limit At the midpoint of the wire is a resistor, in the grid circuit of the radio sonde blocking oscillator The potential developed across the resistor by the discharge therefore controls the pulsing frequency

In all radio sondes for research it is necessary to transmit the air pressure This can be done by incorporating a unit from one of the standard meteorological instruments Most workers have used the variable modulation frequency or chronometric types choice of design is a matter of convenience, depending on the particular problem and method of transmitting the data

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Psychophysical Relationships and their Study

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The main function of the present article is to draw the attention of industrial chemists and physicists to a selection of the psychological literature available on psychophysical relationships and measurements Such problems are being forced, with increasing insistence, upon the attention of workers outside the psychological field If some of the artificial barriers between different departments of human knowledge can be made easier to cross, it will be of advantage to workers on both sides

Psychophysical problems are encountered wherever physical processes have to be considered in relation to their effects on human beings Fundamentally, there appear to be three separate functions to be served by such studies These are

1 Measurement, in physical terms, of the characteristics of human discrimination and its variation, in a variety of fields Included in this will be estimates of sensitivity and any unexpected bias in the human judgement, as compared with the physical standard Extensive work has been carried out on colour and brightness discrimination, discrimination of intensity and pitch of sound, discrimination of pressure and lifted weights Within the last 10 years investigations have also been made of the discrimination of the elasticity of vulcanized rubber and the viscosity of stiff liquids as assessed by handling[1-3] *e g* compression between finger and thumb Studies of complex materials and the comparison of qualitatively different materials (*e g* bitumen versus rubber) have been included[4, 5]

2 Although most measurements of human discrimination are made in laboratory situations or by means of specially designed tests, discrimination of a similar type is required to fulfil some specific function in everyday life Thus colour discrimination is involved in many industries, such as dyestuffs and paint, or in the electrical industries for colour codes Firmness discrimination or the discrimination of rheological (flow and deformation) properties is involved in baking and in cheese manufacture and grading In each instance physical or instrumental measurements may be made where the human judgement is at present used and it is important to determine the relative value of the unaided human discrimination, as compared with the objective measurements, in fulfilling the specific requirements of the control processes or the assessment of the final product

3 Finally, the expression of any formal relationships between physical concepts and measurements and psychological concepts and measurements is a fundamental problem for psychophysical study The 'illusions' probably fall into this category, the term illusion may have arisen as a result of the assumption that there should be a one to one correspondence between an experience or perception (psychological system of classification) and the description of the field of stimuli (physical system of classification) Fundamentally, the perception or the experience is the material from which, by the processes of abstraction and theorizing, underlying physical principles and concepts have been inferred

CLASSICAL PSYCHOPHYSICAL METHODS

The greater part of the psychophysical investigations carried out so far have been concerned with the first of the three problems outlined above[6-8] Sensitivity is generally measured in terms of a 'threshold' which represents the transition point between the stimulus (or stimulus difference) which is too small to detect and one sufficiently strong Although it is generally assumed to be a clearly defined barrier which must be surpassed before a stimulus does elicit any response, the threshold will represent a stimulus (or stimulus difference) which elicits a 'correct' response on a specified proportion of the occasions of presentation The threshold is therefore a statistical unit rather than a functional unit If there is a functional unit it might be that corresponding to a single quantum of energy or small number of quanta. This point has been discussed recently, at some length, by M H PIRENNE[9]

The threshold (or its equivalent) may, then, refer either to the minimum stimulus or stimulus difference, which can be detected (subject to the above restrictions) The first is normally designated the stimulus or absolute threshold, the second is usually termed the difference threshold The stimulus or absolute threshold is complicated by the fact that there is no state corresponding to zero stimulation of the human organism In vision, even with no external stimulus, there is a certain amount of spontaneous retinal activity and in the auditory sphere some spontaneous activity will remain even when extraneous stimulation is removed These remarks apply to composite sense organs *in situ* rather than to isolated single receptor units in single fibre preparations

The precise estimates of the sensitivity of human discrimination are to some extent dependent on the particular experimental techniques used and on the formal processes of calculation There are three principal psychophysical methods Which is used on any particular occasion depends partly upon the limitations imposed by the form of the material constituting the stimuli These methods* are

1 the adjustment method, or method of average error

2 methods of serial exploration

3 frequency methods, some of which may be included under section *2*

In the first method a constant stimulus is presented and the observer adjusts a variable one until he has obtained apparent equality Enough trials are made to determine the average setting and its standard deviation The former gives the observer's bias or 'constant error', the latter indicates the uncertainty of the settings and is sometimes claimed to give an adequate measure of sensitivity

Included in the constant errors are the relative effects of successive presentation (sounds) or relative position (visual stimuli), and whether adjustments are being made by increasing or decreasing the matching stimulus

In the 'method of limits' or 'just noticeable differences' the stimulus is increased by small steps until the observer reports its detection, or, if the difference threshold is being measured, reports that the variable stimulus is greater or less than the standard Both ascending and descending series are used A judgement of three categories is frequently employed when the difference threshold is being assessed, so that a transition point from 'less to equals' and from 'equals to greater' may be assessed. Precautions have to be taken to allow for the effects of suggestion for the observer may anticipate the actual transition point if he has decided that the stimuli are progressively increasing or decreasing. R W PICKFORD[10] describes the method of limits as 'the only psychophysical method sufficiently adaptable for rapid and efficient tests on a large number of untrained subjects'.

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* A further method may, perhaps, be added in which continuous control is maintained on a changing stimulus so as to keep it 'just perceptible'[14]

One of the 'frequency methods' is the 'method of constant stimuli', and in this the comparison stimuli are presented in random order. Where only two categories of response are permitted (greater or less) the relative frequency of judgements of a specified type is calculated. The median stimulus value (*i.e.* corresponding to fifty per cent judgements greater) indicates whether any unusual bias of judgement is present. The standard deviation of the distribution of stimuli with the observed frequencies gives a measure of the sensitivity of discrimination. The constant method with three categories of judgement (greater, equals or doubtful, and less) enables two transition points to be determined, corresponding to the change of judgement from 'greater to equals' and from 'equals to less'. These points will be the median stimuli obtained from the frequency distribution of judgements greater and judgements less, respectively. R S WOODWORTH[11] has remarked that the difference threshold of the method of 'just noticeable differences' is a direct measure of sensitivity since the observer is looking for a transition point and is aware of it when it occurs. The difference threshold of the method of 'constant stimuli' emerges only at the computer's desk.

Probably the most satisfactory statistical method for dealing with data in the form of a two category response is 'probit analysis', outlined by D J FINNEY[12]. This technique is a refinement, developed independently, of the treatment elaborated by G E MÜLLER[13] and F M URBAN[14] from G T FECHNER's[15] earlier work.

SOME FACTORS INFLUENCING MEASURES OF SENSORY DISCRIMINATION

Under this heading are included the effects of the particular method of obtaining the estimate of the sensitivity of sensory discrimination. Practice, fatigue, boredom, habituation or familiarity with the experimental setting all play a part in determining the apparent level of discrimination. Incentives are frequently ignored, but there is evidence to suggest that they are very important. (Knowledge of results may itself be an adequate incentive.) The attitude of the observer, his confidence and temperamental characteristics are reflected in his performance.

Some people show a marked variation in discrimination on different days. Short period changes in sensitivity are more difficult to detect, but there is evidence to suggest that such variations exist. These would be obscured if the observer were allowed as much time as he pleased to make a judgement. The continuous recording technique recently developed by R C OLDFIELD[16] has indicated that as much as a tenfold variation may occur in the visual threshold in a matter of a few minutes. This technique may ultimately be of value in assessing personal characteristics, for it is believed that a person whose judgement oscillates widely in one activity will do so in another[17].

The interaction of qualitatively different stimuli is often overlooked, although it is a common occurrence in everyday life in which our knowledge of the external world is dependent upon the complex spatial and temporal pattern of a variety of stimuli, *e.g.* temperature, touch, taste, colour, brightness, sound. A number of laboratory studies have been made on the interaction of one sensory modality upon another[18,19] and K KEKCHEYEV[20] has recently claimed that the idea of a second stimulus may produce a similar effect to that due to one actually present. Where the stimuli are relatively pure (*i.e.* involve quantitative variation in respect of only one quality or dimension) a more serious source of disturbance to simple relationships is that judgements are made with reference to the previous sequence of stimuli rather than with reference to a single comparison standard[21].

For certain forms of investigation some subjects may have to be discarded owing to extreme variability. The attitude of the subject, particularly whether he is judging analytically or spontaneously, without conscious analysis, may be of considerable importance. Investigations have shown that attitudinal factors can be to some extent controlled by suitable instructions[22]. This, in turn, stresses the need for using written and standardized instructions. If oral instructions are used they may be only partially assimilated and, more seriously, may vary unwittingly from one experiment to another. With naïve untrained subjects it is desirable to give them a few preliminary trials or to consider the first judgements as a practice period. These data may be discarded from the main analysis unless the learning processes are of special interest.

Where stimuli are presented successively for comparison, the 'time error'[23] is of considerable importance. As a rule, the second of two equal weights feels heavier than the first, or gives a larger number of 'greater' judgements. Evidence has been put forward to suggest that this type of systematic bias is dependent upon the magnitude of a particular stimulus and upon the training of the observer[14]. Similarly, the second of two equally intense sounds, separated by a short interval of time, appears to be louder than the first. Examples could be multiplied, although the direction of the time error may be different for different subjects and will alter as the interval between the first and second stimulus is changed.

All threshold measurements are concerned with the detection of small differences. In fact, only those differences for which there is some uncertainty are really of value for the assessment of the sensitivity of discrimination. For this reason suggestion may play an important part in the response of a subject. It is unfortunate that in many of the psychophysical studies carried out the experimenters themselves, or persons familiar with the field of investigation, so frequently have to act as subjects (or observers) as it is normally impossible to obtain the continuous services, and continuous interest, of uninformed persons.

WEBER'S LAW AND FECHNER'S SPECULATIONS

WEBER's law[15] is an expression of experimental observation. If R and $R + \Delta R$ are two stimuli which are observed to be just noticeably different in the statistical sense indicated above then $\Delta R/R$ is approximately constant. However, the value of $\Delta R/R$ is not completely independent of the stimulus value (since $\Delta R/R$ will also be dependent to some extent on the scaling chosen for the physical stimulus) and the law breaks down both at extremely low and extremely high stimulus values. In spite of this, the Weber ratio gives a useful indication of the relative sensitivity of various forms of human discrimination. The following approximate values may be of interest and include estimates for the discrimination of the firmness of deformable materials which have not been expressed in this form before (*Table I*).

Table I Relative Human Sensitivity by Weber Ratio

Source of stimulus	*Approximate Weber ratios* $\frac{\Delta R}{R}$*
Lifted weights	$\frac{1}{50}$
Pressure on finger tips	$\frac{1}{30}$
Light intensity (visual brightness)	$\frac{1}{75}$
Cutaneous pressure	$\frac{1}{7}$
Taste	$\frac{1}{5}$
Sound intensity	$\frac{1}{10}$
Elasticity of vulcanized rubber	$\frac{1}{8}$†
Viscosity of Californian bitumen (newtonian)	$\frac{1}{8}$†
Elasticity (highly motivated and trained subject)	$\frac{1}{15}$†

* These values are approximate central values taken from a number of sources. Values for different individuals may depart considerably from those given, depending on the training, interest and motivation of the observer. There may also be a change in the value of $\Delta R/R$ with the general stimulus level, R.

† The value of ΔR in these estimates refers to a difference which is correctly perceived in 75 per cent of the judgements.

G. T. FECHNER[16] erected on the basis of Weber's law a series of elaborate mathematical deductions which are not considered by most psychologists to be valid. In spite of this, Fechner's speculations are sometimes put forward as representing the accepted psychological viewpoint. Briefly, Fechner equated the 'just noticeable difference' with what he considered to be the 'unit of sensation' and then proceeded to integrate, replacing the finite differences by differentials. Thus, if

$$S = K \frac{\Delta R}{R}$$

by integration

$$S - S_0 = K \ln \left(\frac{R}{R_0}\right)$$

If it is assumed further that $S_0 = 0$ when R_0 is equal to the threshold then complications arise owing to the necessity of postulating negative sensations for stimuli below the threshold, unless the law is assumed to be valid only above the threshold. There are two essential fallacies involved, the more important being the assumption that a sensation is to be regarded as built up from a series of small differences (*i.e.* that sensation increments are alike in quality and can be added), and secondly that the finite differences may be regarded as infinitesimals (WRIGHT[17] has indicated that this difficulty is by no means insuperable). However, regarding the elaboration as enabling the number of 'just noticeable differences' between two stimuli to be assessed and avoiding the morass of verbal differences that trouble the discussion of the question as to whether sensations are measurable[18], Fechner's treatment has proved a useful basis for the quantitative treatment of the subjective intensity of different sounds[19, 20].

CONSTANCY PHENOMENA

Only a passing reference can be made to the whole field covered by 'constancy phenomena' *i.e.* the extent to which the perception of colours, shapes and sizes approximates more closely to their 'normal appearance' than would be expected from the characteristics of the physical stimuli. R. H. THOULESS[21] has developed a numerical expression for these effects, which vary from one individual to another and with their attitudes and training. The constancy phenomena are dependent upon the additional clues such as orientation or illumination conditions, which are obtained in addition to the main stimuli. It is only when illuminated surfaces are degraded by artificial means into points or areas of light that a simple physical specification of such stimuli is reasonably adequate[33].

SOME WIDER IMPLICATIONS

The methods discussed are equally applicable to the study of the human response to stimuli and patterns of stimuli which may be described in chemical terms. Thus many investigations have been reported involving the assessment of taste and odour thresholds. However, the methods of study outlined seem to give results which have extremely restricted application. This may, of course, be an inherent limitation of the experimental method in psychology where, even more than in quantum physics, the processes of observation alter to some extent what is being measured. This situation is not confined to psychological experiments nor to quantum theory. It is a source of difficulty and active controversy where the mechanical or rheological properties of complex materials are concerned. These difficulties and uncertainties are of central importance to the recent attempts to study the relationship between the measurable properties of complex materials on which judgements may be made by handling. The present writer has, in collaboration with others[34-35], recently reported investigations into these problems using the technique of Multiple Factor Analysis originally developed by mathematical psychologists for the analysis of the structure of and relationships between a variety of mental tests.

Where the relative effects of two stimuli of which the difference is considerably in excess of threshold have to be compared, it is not legitimate to extrapolate from the threshold determinations. It is necessary rather to design techniques actually using stimuli of the order of magnitude under consideration and to make, as far as possible, a direct comparison under conditions closely resembling those to which the data may, in practice, be applied. A recent study of the relative sweetness of sugars contains valuable information on this type of problem[36].

One of the ideal functions of tests of sensory discrimination would be to assist in the selection of the best workers for particular occupations. Psychological studies have shown that sensory tests are of extremely restricted value for prediction purposes and that general intelligence and assessments of personal qualities are more useful.

The following comment is of interest on the use of the threshold technique for the selection of a 'taste panel'. 'The underlying presumption here, of course, is that once a panel of the desired acuity has been chosen, unanticipated differences could then be reliably detected by such a panel. It seems to us, however, that herein lies one of the major difficulties which may suppress any undue enthusiasm for the immediate adoption of such procedures, since it has been found in this and other investigations that acuity in respect of one taste characteristic does not necessarily presuppose acuity in others. At least this is the direction in which present available facts point'[37]. Similar comments might be made regarding physically defined stimuli in an integrated skill.

It has been shown that two stimuli must differ by a larger amount if the observer is to indicate the direction of the difference as compared with that required for the mere detection of difference. Probably, if a selective response is required then even greater differences will be called for. In any integrated skill, such as piloting an aircraft, F. C. BARTLETT[38] has indicated that two thresholds are involved, one indicating what the observer can do, the other what he is prepared to do. These may vary independently. During a period of continuous work, the latter shows a progressive decline which can be arrested by the volition of the observer if he is aware of the lowered standard or even by an increase in the difficulty of the task. In the organization of a complex skill a temporal pattern of responses is involved as well as the mere discrimination of differences. The whole process is frequently interactive and has been compared with the operation of a servo mechanism[39]. A stimulus sets up a response and a response a new set of stimuli. The skill is liable to break down when the intricate timing of the succession of stimuli and responses becomes seriously out of phase, as it were, although within broad limits, variation of timing may be permissible. In studying the nature and organization of a complex skill Bartlett has suggested that the key features and the overall time required to carry out a unitary sequence of actions are of greater value than measurements of thresholds or simple reaction times. What these key features are in different instances has to be decided by informed analysis and judgement of each problem on its own merits.

The work of the Cambridge Psychological Laboratories stresses the limited practical value of the determination of sensory thresholds in isolation from the skills into which they are integrated. The concept of the 'indifference range' has been introduced. 'effective stimuli acquire an indifference range within which stimuli change, although they may be appreciated, they do not call for compensating activity'[40]. The indifference range may represent the threshold in its most directly functional terms Corresponding to this aspect of the threshold is the idea of measuring it within the setting of a skilled performance The technique now being developed by Oldfield and outlined earlier seems to have potentialities as an experimental method of studying this problem

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Chemoreceptors and Regulation of Respiration

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The problem of the regulation of respiration is still, we believe, fundamental for the physiological process of pulmonary ventilation It is well known that the respiratory movements are initiated and coordinated by a group of nerve centres the respiratory centre The activities of the respiratory centre are regulated and adapted to the needs of the organism by means of different mechanisms In earlier days it was customary to distinguish between a reflex nervous and a central chemical regulation of respiration, but recent discoveries have shown clearly that this division is no longer exact since a number of chemical regulatory processes also take place through reflex nervous mechanisms. It is therefore better to differentiate between mechanisms regulating respiration on the basis of factors which are responsible for them rather than on the channels through which they are operative[1] It is therefore necessary to distinguish between mechanical factors (respiratory movements) and chemical factors (composition of the blood and local metabolism of nervous tissues) concerned with regulation of respiration In this review only the chemical factors will be surveyed

EARLY RESEARCHES

As early as 1868 E F W Pflüger[2] showed that an increase of carbon dioxide and a decrease of the oxygen content in the inhaled air induce an increase of pulmonary ventilation, a stimulation of breathing In 1882 J Rosenthal[3] came to the conclusion that it is solely, or almost solely, by virtue of its varying oxygen content that the blood does or does not stimulate the respiratory centre In 1885 F Miescher-Rüsch[4] stated that under normal conditions of rest the chemical control of respiration is related mainly to the carbon dioxide percentage in the air of the lungs and in a lesser degree to the oxygen percentage

Experiments by L Fredericq[5] showed in crossed circulation experiments that changes in activity of the respiratory centre are induced by variations of the carbon dioxide concentrations in the arterial blood supplying the perfused head

The researches of J S Haldane and his co-workers[6-8] demonstrated more directly that an increase of the alveolar pulmonary carbon dioxide of about 0 01 per cent is sufficient to increase the resting pulmonary ventilation (hyperpnoea), whereas a diminution of 0 2 per cent in the alveolar carbon dioxide may cause arresting of breathing (apnoea) On the other hand, respiration was found to remain practically unchanged until the alveolar pulmonary oxygen percentage was reduced from the normal 14 to 8 per cent At this concentration of oxygen in the lungs respiration increased markedly These experimental observations led to the conclusion that under normal conditions carbon dioxide acts specifically on the respiratory centre , increase of carbon dioxide in the alveolar air and in the arterial blood stimulates the respiratory centre, while decrease of carbon dioxide inhibits it The increased breathing during oxygen deficiency was also ascribed to a direct stimulation of the respiratory centre

Experiments showed in addition that increase of acidity of the arterial blood stimulates respiration, while increase of alkalinity inhibits it[9, 10]

REACTION THEORIES

In 1911 H Winterstein[11] advanced his 'reaction theory' according to which the activity of the respiratory centre is regulated in all physiological conditions, including oxygen deficiency, by the hydrogen ion concentration in the arterial blood Later experiments showed however that during acute hypoxaemia the arterial blood shifts not to the acid but to the alkaline side[12]

A number of research workers[7, 12-15] demonstrated that the adjustment of pulmonary ventilation by carbon dioxide is not always related to the arterial hydrogen ion concentration and that hyperventilation induced by oxygen deficiency does not always involve arterial acidosis

H Winterstein[16] then advanced his second 'reaction theory' which stated that the chemical regulation of the respiratory centre is dependent on the hydrogen ion concentration within the centre itself and not on the hydrogen ion concentration of the arterial blood In 1923, working on similar lines, R Gesell[17] advanced his 'intracellular acidity theory' which stated that 'the activity of the respiratory centre is fundamentally a function of its own acidity, as opposed to the acidity of the arterial blood, the concentration of carbon dioxide and the direct stimulating effect of lack of oxygen'

According to M Nielsen[18], however, carbon dioxide is the chemical regulator of the respiratory centre by its specific stimulating effect and not by its acid-forming properties Oxygen deficiency hyperventilation is mainly due to changes in the excitability of the respiratory centre caused by the specific carbon dioxide This theory has been adopted by several physiologists In fact, H Winterstein[7] and R Gesell[19] stated that the experimental observations of M Nielsen are, however, in no way opposed to the 'reaction theory', but on the contrary stand in complete agreement with it. These authors thus reject the 'carbon dioxide regulation theory'

CHEMOREFLEX MECHANISM

In the years 1924 to 1935 J F Heymans, C Heymans and co-workers[20-26] discovered the 'peripheral chemoreflex mechanism' of regulation of the activity of the respiratory centre These researches showed the existence of peripheral chemoreceptors located in the aortic and carotid sinus bodies, *glomus aorticum* and *glomus caroticum* These chemoreceptors are connected with the respiratory centre by means of nerve fibres running in the aortic and carotid sinus nerves, *Figure 1* Further experiments showed that increased carbon dioxide or decreased oxygen in the arterial blood caused a stimulation of the respiratory centre by reflex stimulation of those chemoreceptors, while decrease of arterial carbon dioxide resulted in an inhibition of the centre

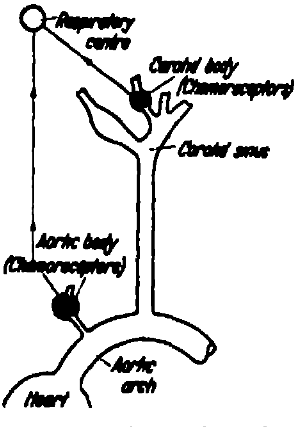

Figure 1 Aortic and carotid sinus chemoreceptors

A selective elimination of the chemoreceptors caused a reduction of pulmonary ventilation by about 36 per cent The chemoreceptors thus exercise a tonic reflexogenic stimulation on respiration[27]. The effects of separation of aortic and carotid bodies demonstrated the subordinate importance of the aortic body as compared with the carotid bodies.

Hyperpnoea provoked by acute oxygen deficiency, which had been previously considered as centrogenic, is now known to be brought about exclusively by the chemoreflex mechanism On the other hand, acute oxygen deficiency directly depresses the respiratory centre itself These experimental observations have been confirmed in the main by a number of investigators[37-40]

In a recent publication C M HESSER[46] points out that the dominating role of the 'chemoreflex drive' in the respiratory defence against acute oxygen deficiency is now firmly established The chemoreflexes are entirely responsible for the hypoxic hyperventilation, at least in those initial stages of oxygen deficiency that are associated with blood alkalosis Consequently those theories must be refuted which state that hyperventilation during acute oxygen deficiency results from the direct stimulating effect of hypoxaemia upon the centre, from increased arterial hydrogen concentration or from increased intracentral or intracellular hydrogen ion concentration in the centre

CHEMORECEPTORS AND RESPIRATORY CENTRE

In the hyperventilation induced by prolonged and chronic oxygen deficiency, the experiments of H BJURSTEDT[45] showed that the initial effect of oxygen deficiency on respiration is exclusively due to the chemoreceptive reflex drive, while the effect of prolonged hypoxaemia is mainly due to direct central impulses In hypoxaemia of long duration, the alkalinity of the blood due to the hyperpnoea progressively disappears At the same time the chemoreflex drive becomes less active and the central drive becomes more and more important, finally controlling respiration almost entirely H WINTERSTEIN[1] has, however, pointed out that, in spite of the reduction of the oxygen saturation of blood during oxygen deficiency, the increase in arterial hydrogen ion concentration induces an increase in oxygen pressure in the blood, which might well be sufficient to explain the decrease in chemoreflex drive during prolonged hypoxaemia In fact, experiments of C F SCHMIDT and J H COMROE[41] showed that the oxygen pressure in arterial blood rather than oxygen saturation is the main factor affecting the chemoreceptors

Records of the action potentials of the carotid body chemoreceptive fibres showed increased impulses with increase of hypoxaemia The great sensitivity of the chemoreceptors to oxygen pressure is further borne out by the fact that such chemoreceptor impulses could be recorded as soon as the oxygen content of the blood fell to less than 96 per cent Increase of oxygen saturation above this level decreases these chemoreceptor impulses[37, 38]

With regard to the role of the chemoreceptors in the regulation of respiration by arterial carbon dioxide, experiments showed that they are stimulated by slightly increased arterial carbon dioxide Records of the action potentials of the chemoreceptive fibres[38] further showed that they began to discharge as soon as the alveolar carbon dioxide pressure exceeded c 30 mm mercury and that the discharge increased approximately linearly in relation to the carbon dioxide pressure Further work[34, 38] showed that even when deprived of chemoreflex innervation, the respiratory centre still responds directly, however, to an increase of carbon dioxide in the inhaled air and in the arterial blood

The importance of the chemoreflexes as compared with that of the respiratory centre itself in the regulation of breathing by carbon dioxide has been much discussed According to one viewpoint, the chemoreflex mechanism plays a significant part in the control of breathing under all circumstances Various workers[30, 33, 37, 39] expressed the opinion, on the other hand, that under physiological conditions the carbon dioxide pressure in the arterial blood also stimulates the respiratory centre through the chemoreflex mechanism, and consequently the chemoreflex component is a necessary factor in the finer adjustment of respiration with respect to carbon dioxide Hyperpnoea induced by carbon dioxide in the alveolar air above the normal 5 to 6 per cent is, according to R GESELL[36], purely centrogenic

The second viewpoint implies that the chemoreceptors are not active under normal conditions and only become so in unusual circumstances typified by anoxaemia, the marked hypercarbia associated with severe respiratory depression, and the action of certain drugs This opinion has, however, become untenable in view of the continually increased burden of experimental evidence indicating that the chemoreflexes are also active under normal conditions Again A PI-SUÑER[48] has attempted, but without success, to revive the old opinion of a pulmonary chemoreceptive reflex mechanism for the excitatory effect of carbon dioxide on breathing

The importance of the aortic and carotid chemoreflex component as compared with that of the direct central component in the regulation of breathing by carbon dioxide under different physiological and pathological conditions is still open to investigation Under some conditions the chemoreflex component may indeed be the most important, while under others the centrogenic component may be predominant These facts have been pointed out recently very clearly by C. M HESSER[46] who stated that 'the chemoreflex drive gains in importance under alkalosis and eupnoea, mainly due to a more marked hypoxic stimulation of the chemoreceptors, and probably to some extent due to an exaggerated effect upon the chemoreflex drive of tissue alkalosis or hypoxia Withdrawal of the chemoreflex component during acidotic conditions reveals that the hyperpnoea during acidosis is mainly centrogenic Under physiological conditions, the chemoreflex component is a necessary factor in the finer adjustment of breathing with respect to carbon dioxide '

RECENT THEORIES

The regulation of respiration thus has to be considered in the light of the 'multifactor theory' of respiratory regulation as emphasized by J S GRAY[40] The interaction between the different factors regulating respiration controls the pulmonary ventilation under different physiological or physio-pathological conditions

The physical reflexes (proprioceptive reflexes of respiratory movements) of respiratory regulation may also interfere with the chemical centrogenic and chemoreceptive reflex regulatory mechanisms of breathing Thus the importance of any factor regulating respiration may vary according to the interference of other factors acting directly or reflexly on the respiratory centre

The question then arises to determine to what extent the discovery of the 'chemoreflex mechanism' of regulation of respiration brings about a re-shaping of the 'reaction theory' This problem has been examined recently C HEYMANS *et alii*[33, 34] showed that acidity stimulates the chemoreceptors, while alkalinity acts in the opposite way It has also been shown[39] that the factor which causes the chemoreceptors to be excited by oxygen deficiency and carbon dioxide variations is the hydrogen ion concentration within the chemoreceptive cells themselves

H WINTERSTEIN[1], after summarizing the results of all the recent investigations performed by different authors, proposes the following picture of chemical regulation of respiration The activity of the respiratory centre goes entirely parallel with the reaction of the blood and as far as haematogenic regulation of breathing is concerned agrees completely with the 'reaction theory' The effect of lack of oxygen is entirely reflex by way of the chemoreceptors, the activity of which, again in complete agreement with the 'reaction theory', depends on the intracellular hydrogen ion concentration in the chemoreceptive cells The chemoreceptive regulation of respiration in hypoxaemia leads to increase of alkalinity of the blood on account of the induced hyperpnoea This increase of alkalinity for its part reduces the oxygen pressure of the blood for the same oxygen saturation, thus again increasing intracellular hydrogen ion concentration in the chemoreceptive cells and consequently reinforcing hyperpnoea by chemoreflex drive Thus the sensitivity of the respiratory centre and of the chemoreceptors to any variation in hydrogen ion concentration may explain the changes in respiration induced by carbon dioxide and by hypoxaemia

In the opinion of C M HESSER[46] experimental evidence favours the 'intracentral acidity theory' for direct chemical stimulation of the centre itself The peripheral chemoreceptors probably respond more rapidly than do the central chemosensitive cells (respiratory centre) to changes in arterial hydrogen ion concentration

The possibility of a specific direct action of carbon dioxide on the chemoreceptors and the respiratory centre, besides the action regulated by hydrogen ion concentration is, however, still open for discussion and investigation

J F and C HEYMANS *et alii*[36, 38] showed that the aortic and carotid sinus chemoreceptors are also sensitive to a number of drugs Lobeline, nicotine, acetylcholine, cyanide *etc* stimulate the chemoreceptors and induce a reflex hyperpnoea, while the same drugs do not slightly stimulate or even directly depress the respiratory centre itself These experimental observations have been confirmed[30, 31, 39, 41, 42, 51, 55] The stimulation of chemoreceptors by drugs is not dependent on hydrogen ion concentration but is induced by a direct action of the drugs on the chemoreceptors as shown by U S VON EULER, G LILJESTRAND and Y ZOTTERMAN[39]

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Electrical Properties of Muscle Fibre

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THE speed of action and the power of muscles present one of the most interesting problems of physiology, the ultimate explanation of which will depend upon a thorough knowledge of the contractile material, and especially of the physical and chemical properties of the long-chain protein molecules, embedded in muscle fibres[1-4] It is clear that the development of muscular speed requires more than a suitable arrangement of contractile molecules there must also be a mechanism whereby the whole of a muscle fibre, say 0 1 mm thick and a few centimetres long, is excited promptly and thrown into effectively synchronous action whenever a nerve impulse arrives at the microscopic contact region of the muscle fibre *i e* at the motor endplate Such synchronous action is brought about by a wave of electrical excitation which travels rapidly along the fibre surface, and which closely resembles the action potential by means of which signals are transmitted in nerve fibres The mechanism of this propagation is intimately connected with the surface membrane of the cell and is associated with critical changes of its ionic permeability

It is an interesting fact that nerve and muscle fibres, in spite of their different functions, share the important property of an electrically excitable membrane of being able to transmit impulses from end to end In the nerve fibre this mechanism provides an effective communication signal between distant cell units In the muscle fibre the impulse serves to stimulate the contractile substance all along the fibre, contraction following the action potential wave at every point as it sweeps past In both instances the special function of the surface layer of the cell ensures that a disturbance at one point is rapidly conducted over the relatively long distances of the cell

This review is concerned mainly with the properties of the muscle fibre membrane and in particular with some of its electrical characteristics which have recently been measured It is instructive to compare the membrane properties of nerve and muscle fibres, for the common features of these two types of cell may well apply to excitable membranes in general, while any characteristic differences in their electrical reactions might provide a clue to the unknown process whereby excitation and contraction are coupled

EVIDENCE FOR A SURFACE MEMBRANE

It should be emphasized that no direct way has yet been devised of making the excitable surface membrane of a nerve or muscle fibre visible All known methods of demonstrating this membrane are indirect, but to challenge its existence would be as difficult as to contest the reality of atoms or electrons The 'excitable membrane' is, in fact, a postulate which has been established by a careful study of the chemical composition and electrical behaviour of the cell

Nerve and muscle fibres contain aqueous salt solutions which take up the greater part of the cell volume and are in osmotic equilibrium with the surrounding body fluid, but differ greatly from it in their electrolyte content[5-7] In the outside fluid, about ninety per cent of the osmotic balance is made up by sodium and chloride, while in the internal fibre water these ions account for less than ten per cent of the balance, potassium taking the place of sodium, and organic anions—which still await chemical identification[6]—replacing chloride It has been argued that potassium might have a special affinity to the cell proteins and be accumulated in a 'bound' state rather than as free ions, but the osmotic balance sheet[6, 8] as well as the electric conductivity of the muscle fibre[10 11] make it improbable that the activity and mobility of the intracellular potassium are very much lower than in an ordinary solution There is evidence that the differences in ion concentration between cell and surroundings are maintained, with only a slight expenditure of energy, by a membrane which is much less permeable to sodium and to the internal anions than to potassium and chloride, E J CONWAY[6, 12] has suggested that the main factor determining this differential permeability is the size of the hydrated ion This view has not been universally accepted[7, 14], but it agrees satisfactorily with many findings on living nerve and muscle[13, 15-17]

While there is good reason to believe that potassium and chloride can penetrate the fibre surface more readily than can sodium and organic anions the process is nevertheless very slow compared with that of free diffusion Recent experiments with radioactive tracers[18-20] have shown that the mixing of external and internal potassium takes some hours to reach half-completion, by comparison the same degree of mixing in a 100 μ fibre of agar jelly would take less than one second If we accept the view that the internal potassium ions are freely diffusible within the boundaries of the cell, the slowness of their exchange with external labelled ions is strong evidence for the existence of a special surface barrier

A similar conclusion has been reached by electrical studies These have shown that the interior of nerve and muscle fibres behaves rather like an ordinary electrolyte, of somewhat lower conductivity than the surrounding body fluid, but that the cell surface contains a layer of high direct current resistance and large capacity In other words, the fibre resembles in its electrical structure a miniature cable embedded in the lymphatic tissue fluid

'ACTIVE' AND 'PASSIVE' ELECTRICAL PROPERTIES

The electrical behaviour of an excitable cell is, however, much more complicated than that of an inert piece of cable The normal nerve or muscle fibre contains a chemical source of energy which helps to preserve a steady state and to maintain a low internal sodium concentration against small continuous leakage[7, 18] The surface membrane is thereby maintained at a voltage of 50 to 100 mv, positive outside, and any leakage of potassium and chloride is thus prevented Moreover, the electrical properties of the membrane are altered in a characteristic manner when a current passes through it, and under critical conditions the surface becomes excited and yields a propagating action potential

It has been customary to distinguish between the passive cable properties of the resting fibre and active electrical phenomena which depend upon the internal energy resources of the cell, though it is recognized that there is no sharp division between these two properties and that they are equally important for the transmission of impulses

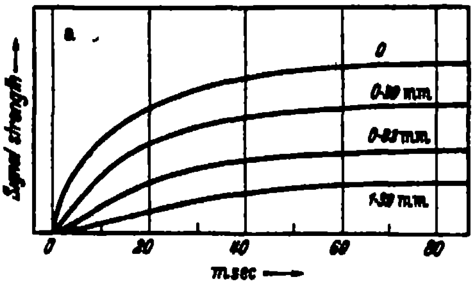
In all these respects there do not appear to be any essential differences in the reactions of nerve and muscle membranes both become excited at those points where the electric current leaves the fibre *i e* at the cathode, excitation occurs when the potential across the membrane has been reduced sufficiently and manifests itself in a rapid progressive lowering of the surface potential followed by a return to the resting level, the so-called 'spike' The electrical cycle runs to completion in one or a few milliseconds It has an explosive 'all-or-none' character in each individual fibre and is capable of generating local currents sufficient to re-excite the neighbouring resting regions of the fibre with an ample safety margin[21-23] The signal travels with constant strength and speed to the ends of the fibre, leaving it ready to respond again after a brief 'refractory period' of one or a few milliseconds

It is clear that this process of transmission differs from that in an inert electric cable in that the signal of a nerve or muscle fibre is boosted to full strength at every point of the line by a local relay mechanism and derives its energy from the local resources distributed along the transmission line, while the message in an ordinary cable obtains its energy usually at its point of origin alone It will be easy to understand the need for a continuous relay mechanism along physiological transmission lines if we examine their electric characteristics quantitatively

If an external electric signal, say a rectangular current pulse, is applied to the surface of a nerve or muscle fibre through two electrodes, and provided that the strength of the current is well below the threshold of excitation, the cable properties of the fibre can be measured[14, 15] A fraction of the applied current penetrates the fibre and in so doing it establishes a potential difference across the fibre membrane This potential difference then spreads along the fibre in the same way in which an electric signal is transmitted along a cable it travels as far and as fast as the leakage and capacity of the cable sheath, in this case the surface membrane, permit By a series of observations which include measurements of the resistance and diameter of the fibres, and of the attenuation and distortion of the wave form in the extrapolar region, the relevant constants such as leakage and capacity of the membrane and conductivity of the cell fluid can be determined

Table I gives a summary of the results obtained from various types of non-medullated nerve and muscle[12] at a temperature of approximately 20°C *Figure 1* shows an example of such measurements the applied signal is a rectangular current of instantaneous rise, the waveform becoming so distorted and rapidly attenuated as it spreads along the fibre that even at 1 mm from its origin it has little resemblance to the applied pulse, and after a few millimetres no detectable signal strength is left

We must conclude, therefore, that as passive cables our nerve and muscle fibres would be useless A message which depended, as in an inert cable, solely upon the energy supplied at its origin would not travel far In addition, it is clear that a relay mechanism is required to boost the signal to full strength at every point of the fibre and so ensure its propagation without decrease The reasons for the 'defective' properties of our physiological cables are obvious their core is not composed of thick strands of copper, but of a thin filament of jelly containing a dilute salt solution, and their sheath does not consist of a few millimetres coating of insulating material, but rather of a delicate and porous lipoid layer, perhaps not more than two molecules across[16]



a *Preparation consisting of two frog muscle fibres, diameters 190 and 50μ*

Figure 1 'Passive' spread of a sub-threshold electric signal in nerve and muscle fibres The applied signal was a rectangular current of instantaneous rise, this signal is recorded from the surface of the fibres at various distances from the point of application

b *Single crab nerve fibre, outside diameter 43μ*

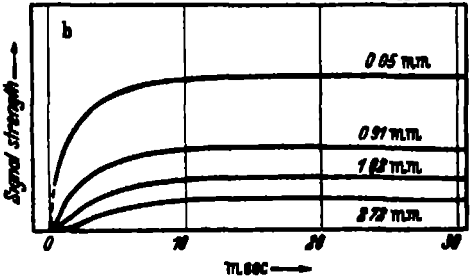


Table I Electrical Constants of Nerve and Muscle Fibres

Fibre type	*Diameter* μ	*Characteristic length of fibre* mm	*Time constant of membrane* msec	*Transverse resistivity of membrane* Ω × cm²	*Membrane capacity* μF × cm⁻²	*Specific resistivity of fibre interior* Ω × cm	*Specific resistivity of outside fluid* Ω × cm	*Reference*
Squid nerve	500	2 5	0 7	700	1	30	22	64, 65
Lobster nerve	75	1 5	2	2,000	1	60	22	24
Crab nerve	30	2	5	5,000	1	60	22	12, 28
Frog muscle (bundles of adductor magnus)	75	0 7	9	1,500	6	200	87	12
Frog muscle (extensor digit IV)	45	1 1	18	4,000	4 5	260	87	12

Nevertheless the passive cable properties of nerve and muscle play a very important part in the transmission of impulses They provide the electric link between adjacent regions of the fibre and ensure that electric currents generated by the activity of one region will spread over a small distance into the resting region, sufficient to excite its relay mechanism[31] It has been observed that changes in the electric circuit constants *e g* in the resistance of the fluid surrounding the fibre, alter the velocity of the impulse in a manner which can be calculated on simple theoretical assumptions[37, 38] Furthermore, there is a correlation between the cable constants of different fibre types and their conduction velocities the lower the internal resistance and the smaller the capacity of the surface membrane, the higher the speed of the impulse, this probably explains why large fibres of the same animal conduct more rapidly than small fibres[31], and why muscle fibres of which the membrane capacity is high conduct more slowly than nerve fibres of which the membrane capacity is relatively small[18]

TRANSMISSION IN MEDULLATED NERVES

It should be pointed out that these comparisons cannot readily be extended to the medullated nerves of vertebrates, for the structure of these nerve fibres is more complicated They possess a relatively thick accessory sheath which is broken at regular intervals, at Ranvier's nodes Apparently an exchange of ions between fibre and surroundings can occur only at these nodes, where the nerve membrane itself is exposed, and there is good reason to believe that the active relay process is restricted to these nodal regions[39] It seems that, in medullated nerves, impulses travel from node to node by means of the ordinary cable mechanism without local energy supply, and that they are boosted only at the discrete nodal regions, every 1 to 3 mm apart It would appear that this is a more economical type of transmission than that in muscle or non-medullated nerve, but it must be admitted that even in these tissues the transmission of signals proceeds with extraordinary efficiency and with only a very minute dissipation of energy[33], the heat produced during the transmission of one million impulses along 10 cm of a crab nerve fibre being only of the order of one μcal

TIME CONSTANT OF MUSCLE FIBRE

One of the interesting points arising from the results of *Table I* is that it provides an explanation of the large electrical time constant of the muscle fibre Electrical stimulation of muscle[34, 35] has revealed that its time factor of excitation is of the order of 10 msec, much longer than that of its motor nerve Furthermore, it has been shown that a motor nerve impulse which lasts only about 1 msec produces a local potential change at the endplate region of a muscle fibre which takes 20 to 30 msec to decay[35] One of the reasons for this difference in time scale appears to be the large capacity of the muscle membrane, the latter being able to retain applied electric charge for many milliseconds

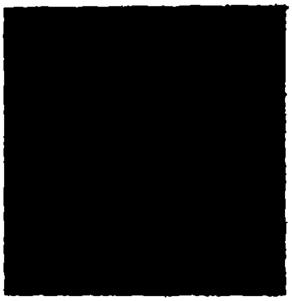


Figure 2 Action potential recorded between inside and outside of a squid nerve fibre[40] The vertical scale indicates the potential of the internal electrode in millivolts, the outside fluid being taken as at zero potential During activity there is a reversal of the potential difference across the membrane Time marks 500 c/s

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The physical significance of this large capacity remains to be explained it may be due to a genuine difference between nerve and muscle membranes, but alternatively it has been suggested[17] that the muscle membrane might be 'in folds', rather than in an expanded state, and that the large value of its capacity might be only apparent and, in reality, arise from an enlarged surface/volume ratio

NATURE OF THE MEMBRANE RELAY MECHANISM

It has been found possible in recent years to study the electrical properties of the cell membrane by inserting small electrodes inside the fibre, so recording the potential difference between inside and outside directly across the membrane without extraneous shunting Experiments of this kind have been made on the giant nerve fibre of the squid[40, 41], see *Figure 2*, and on frog muscle[42–44] and have given the following results

The resting membrane is charged to 50 to 90 mv, outside positive This resting potential is a function of the external potassium but is independent of the external sodium concentration During activity the potential difference across the membrane is temporarily reversed to 30 to 50 mv, outside negative The reversed swing depends greatly upon the external sodium concentration, it becomes larger if the sodium concentration is raised and disappears if the sodium content is reduced to less than one third[41, 45] A similar effect has been observed in other nerves and in muscle fibres[42, 44], but in the latter the waveform of the action potential is different, there being a slow monophasic, instead of diphasic, return of the potential wave The theory has been advanced[46] that the resting membrane is relatively impermeable to sodium, and that the active cycle is

Figure 3 Action potential and membrane impedance change in a squid nerve fibre[50] *The white line shows the action potential as in Figure 2, the white band represents the transient increase of the membrane conductance, registered by the transient unbalancing of an alternating current bridge Time marks. 1,000 c/s*

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accompanied by a transient increase of the sodium permeability It is thought[47] that the membrane contains special molecules which are negatively charged and can act as 'sodium carriers' The resting potential itself stabilizes the position of these molecules, but the reduction of the resting potential by local action currents releases their movement and thereby allows some sodium ions to traverse in the direction of their concentration gradient Thus sodium enters the fibre and reduces the resting potential further in this way an electrochemical chain-reaction is initiated which involves the transfer of a minute quantity of sodium into the fibre and the extrusion of a minute amount of potassium in exchange This view is supported by direct observations of the rate at which radioactive sodium and potassium tracers move across the fibre surface during periods of rest and activity[48, 49] It appears that the quantities of cations which are exchanged during activity are of the right order of magnitude-*i e* they are large enough to account for the electric current strength of the propagated spike

It is interesting that the active phase of the impulse is accompanied by a sudden reduction of the electric impedance of the membrane, *Figures 3* and *4*, an effect which has been attributed to an increase of its ionic permeability[50, 51]

DIFFERENCES IN ELECTRICAL REACTIONS OF NERVE AND MUSCLE MEMBRANES

In all the above respects nerve and muscle fibres appear to function in the same manner, in certain details, however, important differences are seen The differences in time scale and in the size of the membrane capacity have already been mentioned Another distinction is the shape of the action potential of muscle fibres[52–54], this shows after the main spike a large residual depolarization, or '*negative after-potential*', which subsides only slowly It may be that this slow phase is related to the next event in muscle functioning, namely the activation of the contractile mechanism

Further, a peculiar difference between frog muscle and non-medullated nerve is found when both are exposed to a high external potassium concentration As mentioned above, the internal electrolytes of the fibre consist mainly of potassium, which can penetrate the surface membrane, and of organic anions, which cannot penetrate It is possible to imitate this condition on the outside of the muscle fibres by immersing them in a solution of potassium sulphate *e g* 0 06 M potassium sulphate to which 0 05 M sucrose is added Sulphate, in contrast to chloride, is known not to penetrate the fibre surface[55] The muscle becomes completely depolarized and inexcitable in this solution, but it is not permanently damaged and recovers when returned to more normal surroundings[56, 57] It would be expected that, under these conditions, any electric current which passes through the membrane is carried by potassium only, and as the potassium concentrations are approximately the same on either side that the resistance would be independent of the direction of the current The membrane, however, in fact shows a very striking rectifier effect, the resistance at the cathode *i.e* to outward currents, being many times greater than at the anode, where current enters the fibre. Evidently the electrical conditions on either side of the fibre surface are not symmetrical, and it appears as though potassium can be made to enter the fibre more easily than to leave it It may be that the structure of the muscle membrane is 'asymmetrical' and that, in the course of the outward current flow, a rapid depletion of potassium occurs at the inner surface At any rate

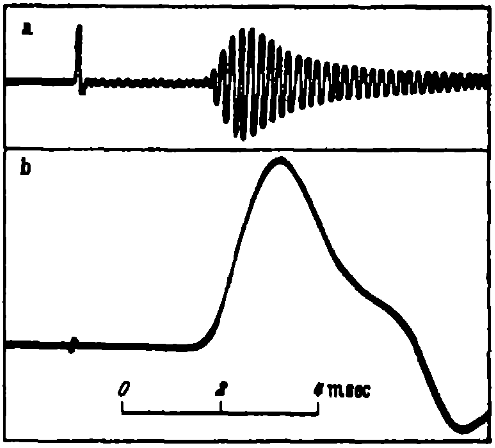

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Figure 4 Action potential and membrane impedance change in a frog muscle[51], *cf Figure 3 The upper record shows the transient unbalance of the alternating current bridge although the oscillations in the first part of the trace have been lost in reproduction, and the lower record shows a muscle action potential (diphasic lead)*

the observed effect is striking, and it is interesting that no trace of it has been found in Carcinus nerve fibres, which lose all rectifier action and tend to become irreversibly damaged when they are exposed to a high concentration of potassium sulphate

DEPOLARIZATION OF ENDPLATE AREA

In dealing with the electrical properties of the muscle fibre we have, so far, neglected the specialized region in the neighbourhood of the nerve contacts, the motor endplate The mechanism by which impulses are transmitted from nerve to muscle goes beyond the scope of this article, and it must suffice to refer to the recent discovery that acetylcholine, $C_7H_{17}O_3N$, is released at the nerve terminals[38] and that it depolarizes specifically the endplate area of the muscle membrane[39-41].

It will be of great interest to inquire into the mechanism of this special chemical depolarization It may be that the acetylcholine ion itself is able to penetrate the endplate membrane at such a high rate that it produces a local depolarization ; alternatively, acetylcholine might render the endplate region more permeable to sodium and thus, indirectly, initiate a local electromotive change

It has recently been shown by P FATT (unpublished) that acetylcholine depolarizes the motor endplate even in the absence of sodium , this finding eliminates the second possibility mentioned above

RELATIONSHIP OF ELECTRICAL TO MECHANICAL CHANGES

Finally, a word might be said as to the relationship between the electrical changes of the muscle membrane and the ensuing mechanical changes of the fibre There is little doubt that the contraction is a local sequel to the action potential wave[42] but the mechanism of coupling between these two phenomena is unknown It has been suggested that the transport of ions through the muscle substance might initiate the contractile cycle, but it is more likely that the process starts at the fibre surface and quickly spreads inward at every point The argument is as follows if an electric current is passed through a muscle from end to end contraction does not commence at the same instant throughout , an excitation wave is initiated at the cathode, however, and the contraction follows the action potential in its course along the fibre If the propagation has been stopped, by a drug like cocaine or by withdrawal of sodium, a strong enough current will still produce contraction, but only locally in the neighbourhood of the cathode It is clear, therefore, that the contractile substance is not stimulated by the flow of current as such, except possibly at those points where the current leaves the fibre

It can further be argued that the stimulus which mobilizes the contractile matter is not the flow of current at all but the diminution of electric charge density at the fibre surface · first, because it is doubtful whether a brief electric current would affect the distribution of ions in the fibre except at its surface membrane, and secondly because contractions can be produced by chemical depolarization without any current flow[43] Certain chemical agents *e g* potassium and veratrine ($C_{32}H_{49}O_9N$), cause a diminution of the resting potential associated with contracture Contractures of this kind are rapid and reversible , they can be made to summate with the effects of cathodic, depolarizing currents and to relax under the influence of anodic, repolarizing currents These contractures share an important feature with the local electric contraction at the cathode and with the normal muscle twitch in that they are associated with a loss of electric charge of the fibre membrane This electric alteration, therefore, appears to be the one most intimately connected with the initiation of the contractile cycle, though it must be admitted that the next link of the process is, at present, completely mysterious

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Irrigation Requirements in Spain

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CONDITIONS of climate and soil typical of Spain lend to its agriculture certain specialized features which differ entirely from those found in England, and indeed lie in direct contrast The differences may be summed up as follows high temperatures and low humidity in Spain and, on the other hand, abundant humidity and low temperatures in England

These well known facts are of great consequence for us Not only must we contend with large expanses of poor soil characteristic of dry climates but our success in agricultural development is further limited by deficient water supply due to lack or inadequate distribution of rainfall Given adequate water, and taking into account the warm climate, there are enormous possibilities for arable farming This is the crucial factor which makes development of irrigated land in Spain essential* But the hydraulic resources of the rivers are limited and water must be controlled in a manner which will ensure maximum harvests i e only the quantities strictly necessary for the needs of the crops must be used, so that the benefit of the irrigation is spread over the widest possible area This concern has prompted the recent establishment of a small network of lisimetric stations, under the joint control and maintenance of the Higher Council for Scientific Research and the National Institute of Agricultural Research of Spain Since it is necessary to know as accurately as possible the evaporation and transpiration rates of the various crops during the whole course of their development, we have adopted the well known gravimetric method whereby the plants are grown in lisimeters which are weighed periodically with suitable precision balances, thus determining the amount of water evaporated and transpired in a fixed period of time by the differences between corresponding readings

There are at present ten stations of this type They constitute an organization which covers the principal regions of Spain The sites of the stations are as follows North region, Pontevedra , Ebro Basin, Saragossa and Binéfar , Douro Basin, Valladolid , Central region, Madrid and Alcalá d. Henares , Eastern region, Valencia , Western region, Badajoz , Southern region, Seville and Málaga

The oldest station is that at Binéfar (Huesca) and was established by the Ebro Conservancy Board. Then came the two in the Central region, and that of Seville, which began operation in 1945 and 1946.

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* The National Hydraulic Works Plan, which is now in progress, is aimed at placing some 900,000 ha under irrigation.

Those of Valencia, Badajoz and Málaga were completed in 1949, and those at Saragossa and Valladolid will be completed this year.

DESCRIPTION OF INSTALLATIONS

These are composed of two essential elements: a group of mobile lisimeters arranged in double rows, and between them a travelling balance provided with a crane.

As regards the type of lisimeter, it has been decided to use cylindrical tanks of uralite which combine various advantages: they are chemically inert with respect to the soil, they are light, easy to obtain and replace, and more economical than most other devices. The inner surface is waterproofed, and at the lower end of one side is an orifice closed with a rubber bung for the removal of drainage water.

Two types of lisimeter have been adopted, the smaller of 36 cm internal diameter and 70 cm high, the larger of 53 cm internal diameter and also 70 cm high. It is convenient to employ two types with different dimensions, since some relatively tall plants, such as maize, have an extensive area of growth and require large masses of soil. With these it is not possible to grow more than one plant per lisimeter since the large containers have a soil area of 0·22 m^2. On the other hand, the smaller type, having a soil area of 0·10 m^2, can take several winter cereal plants, or one plant each of haricot bean, French bean, beetroot *etc*.

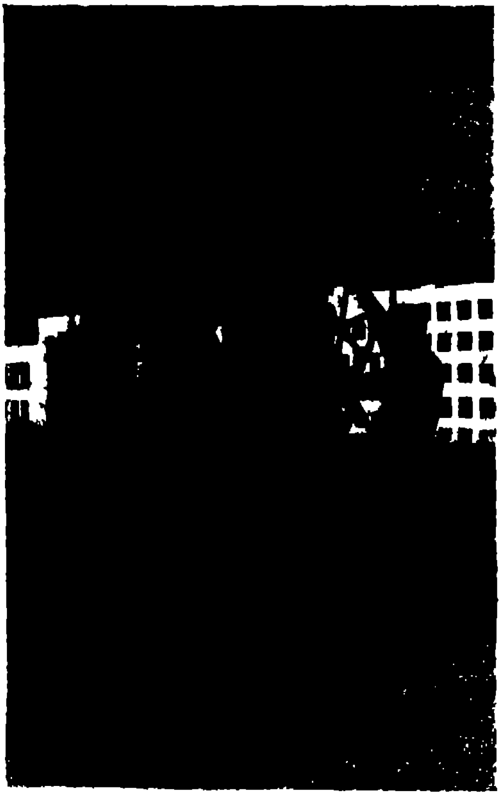

Figure 1 *Lisimeter in operation*

In all the lisimeters the contents are arranged in the following way: at the bottom, a layer of coarse gravel, then layers of progressively finer gravels, ending with one of very fine shingle 15 cm above the base; above this final layer the remaining 55 cm is filled with fertile soil. This arrangement gives an adequate depth of soil and also leaves space, amongst the coarse gravel, for the accumulation of drainage water, which is easily removed, as described previously.

In spite of this an experimental error is unavoidably introduced by isolating a quantity of earth from the rest of the soil although the quantity is large (85 to 90 kg in the smaller lisimeter, 175 to 180 kg in the larger). Another less easily avoidable error is introduced by variations in soil temperature across the uralite walls. In order to reduce this as much as possible the lisimeters are kept in the ground in cylindrical brick-lined cavities, the diameter of which is slightly greater than that of the lisimeter. In this way the walls are protected against direct sunlight and are nearer to the natural layers of the soil in the plot, thus favouring better temperature equilibration.

The lisimeters are arranged in paired rows, with a mobile carriage bearing the balance between them. This apparatus, so essential to the installation, has been the subject of prolonged study: an arrangement had to be contrived which would carry, in addition to the balance, a crane for lifting the lisimeters out of their positions in the ground and keeping them suspended during removal of drainage water. At the same time it was necessary to ensure great precision and sensitivity in the balance, simplicity in its use, and lightness of construction so as to obtain a minimal weight, and thus easy and rapid transport and manipulation.

All this has been achieved in an apparatus (of which *Figure 1* gives an idea) which in all its constituent parts is a product of our national industry. Among the essentials of the apparatus is the carriage which is provided with four wheels, of which the front pair is for steering and is attached to a bar and collar arrangement so that a single man can move the vehicle in any desired direction. On the carriage is a revolving platform carrying the balance, the crane and a large box for counterweights.

The arm of the balance is eccentric to the rotating platform so that the weights do not project over the lisimeters during readings but over the ground, while the other end necessarily extends over the centre of the lisimeter The weighing operation is simple and rapid, it consists essentially of hooking the suspensory mechanism on to the lisimeter and inclining towards it the arm of the balance Weights are then loaded on the opposite arm until they are sufficient to raise the lisimeter and maintain it suspended, lifting it only partially from its position in the ground Once the weighing is completed it is easy to disconnect the mechanism and return the weighed lisimeter to its place

Figure 2 Mobile weather shield to admit light and air while excluding rain from plants

The degree of accuracy of the weights is of the order of 5 gm when working with the small lisimeters and of 10 to 15 gm with the larger type This high sensitivity permits readings of great precision which are useful *e g* in order to ascertain the daily variations in transpiration at as short an interval as required

OPERATION OF THE STATIONS

In each station is studied the water consumption of the plants which constitute the most important crops of the particular region At the moment these observations are carried out on the following plants

Northern region	maize, potatoes, purple clover*
Central region	wheat, barley, oats, maize, alfalfa, broad beans, French beans, sugar beet, tomatoes, cabbage
Eastern region	wheat, maize, French beans, potatoes, onions, groundnuts
Western region	wheat, barley, maize, broad beans, French beans, vetch, tobacco, cotton, cabbage
Southern region	maize, cotton, sugar cane, Spanish sweet potato, alfalfa, clover

Maize is thus the control plant which serves to establish comparisons between the effects of the climates of the different regions acting on the same crop Other plants, such as wheat, potatoes *etc* are also grown in more than one station for reasons of interest and for their importance in the agriculture of the region concerned

The planning of the experiments varies but a minimum of three experiments on each crop is carried out per year The first consists of submitting the plant to an atmosphere lacking in moisture, the second of admitting only the moisture which is strictly necessary to the plant, replacing at suitable intervals the water lost by evaporation and transpiration, the third consists of giving more frequent and generous waterings than in the second experiment Each procedure is carried out in three or four lisimeters and therefore at least nine to twelve lisimeters are needed per plant per year to perform three experiments with three or four repetitions.

Nevertheless the number of experiments is usually greater than this, for example, in cereals the development is divided into three periods the first from sowing till formation of shoots, the second up to the beginning of ear formation and the third up to the complete ripening of the grain In each of these periods water is either withheld or supplied in excess, resulting in the following seven experiments

1 deficiency of water in the first period
2 deficiency of water in the second period
3 deficiency of water in the third period
4 excess of water in the first period
5 excess of water in the second period
6 excess of water in the third period
7 water equilibrated in all three periods

Excess moisture is easily produced by means of watering On the other hand, to produce moisture deficiency in crops growing during the autumn and winter a device is required which will shield them from rain but not keep out the light This is achieved by means of mobile glass covers in wooden frames which form small shelters completely covered on the two upper surfaces, partially open at the sides and completely open at the bottom so as to provide free circulation of air around the plants, while rain is prevented from entering Such an arrangement is shown in *Figure 2*.

Table I Relationship between Water and Dry Matter Formed

Data	*Constant water in the three periods*	*Lack of water in the three periods*					*Excess water in the three periods*			*Units of measurement*
		First	*Second*	*Third*	*First and second*	*Second and third*	*First*	*Second*	*Second and third*	
Irrigation in first period	2,881	1,806	2,881	2,881	1 806	2,881	3,956	2,881	2,881	m³/ha
Irrigation and rain in second period	2,409	2,538	1,291	2,538	1,291	1,291	2,538	3,656	2,538	m³/ha
Irrigation and rain in third period	651	480	480	308	480	308	480	480	1,297	m³/ha
Total of rain and irrigation	5,942	4,824	4,652	5,727	3,577	4,480	6,974	7,017	6,716	m³/ha
Total water evaporated	6,044	4,426	4,857	5,623	3,374	4,779	5,857	6,351	5,544	m³/ha
Wt of plants without grain	12,906	11,524	9,288	9,072	8,858	12,384	8,436	18,490	14,680	kg/ha
Wt of grain	3,010	1,935	1,804	4,366	903	516	—	6,090	4,790	kg/ha
Total dry matter	13,145	11,013	8,562	11,206	7,948	10,021	6 623	20,252	15,987	kg/ha
Kg water evaporated per kg dry matter formed	460	402	567	502	472	477	884	314	347	—

In the first experiments in which this arrangement was used it was observed that temperature abnormalities were produced by protecting the plant from night cold This effect was very marked when the covering was in position day and night during the period in question, but became negligible when the arrangement was used only in daytime while the rain lasted, and left off at night except at times when the sky was completely clouded over and rainy Naturally, the days and times of day at which the covering was used were carefully noted These observations taken in conjunction with the rainfall readings permit exact calculation of the amounts of water received by the plant

As for the general technique of the experiments, this consisted of keeping a numerical record for each lisimeter, noting the treatments applied and the principal details of the crop and its growth, observing weights, quantities of water from rain, irrigation and drainage, and thus establishing a true picture of the water balance over the whole crop

Given the considerable number of lisimeters which must be kept in operation, it is not possible to weigh them all daily, but only once or twice per week More weighings would not be of use, since replacement of evaporated water is conveniently performed at intervals of a few days so that the quantity given will be large enough to reach the depth necessary in fertile soil

Nevertheless, it is usual to weigh one lisimeter daily for each crop, in order to establish correlation between the meteorological observations, which are of course issued daily, and the daily results for the evaporation and transpiration rates of each crop.

INTERPRETATION OF RESULTS

The interpretation is surely the most interesting and delicate point of this work, if conclusions are to be derived from it with a practical bearing on agriculture and particularly on water requirements and supply It is not possible, in general, to use figures from three or four single lisimeter experiments to obtain information on large scale cultivation simply by multiplying the results by the number of plants normally present in a hectare Such a basis of calculation would apply only when the plants in the lisimeters grew according to the average of those in the field But, on the other hand, it is reasonable to conclude that in the open country as in lisimeters a relationship exists between plant development and evaporation-transpiration rate, and that within certain limits the amount of the yield is in direct proportion to the amount of water transpired This fact is thoroughly demonstrated in the lisimeter experiments and serves as a basis for calculation *Table I* shows the relationship between water and dry matter formed

The author has recently published an article on the cultivation of potatoes in the Central region[1] explaining and justifying this hypothesis by means of comparisons between results obtained in lisimeters and in cultivated plots We shall see these same theories applied to experiments with maize The results of this and of eight other experiments, carried out at the same time but with different degrees of humidity, are also given

The first part of the summary of the above article is compiled using figures obtained by the multiplication of lisimeter results by 43,000, the number of plants present approximately in a hectare, and in the same way the quantities of water and the weights of the yield are adjusted to hectare values. The last part of the summary simply relates the weights of water administered to the yield obtained, expressed as usual in terms of dry matter If we limited ourselves to using the results calculated per hectare, we would have to admit that in order to obtain a yield of 6,000 kg of grain the most advantageous volume of irrigation is about 7,000 m³ (experiment with excess water in the second period) It is a fact, however, that a good harvest may be about 3,000 kg/ha This shows clearly that the plants corresponding to the first experiment (with water approximately constant and equilibrated throughout the whole period of

Table II Ratio between Water Evaporated and Dry Matter Formed

No of days	*Stage of development*	*Mean daily evaporation*		*Evaporation in period m³/ha*
		Per plant gm	*Per hectare m³*	
22	From sowing to first watering	198	8 5	187
7	Following first watering	1 164	50 0	350
18	Prior to flowering	2,546	109 5	1,971
13	From male flowering to appearance of ear	2 491	107 1	1,392
15	From appearance of ear to nipping-off of male flowers	1,945	89 6	1,254
15	Following this operation	781	33 6	504
16	Last stage of life	558	24 0	384
			Total	6 042

growth) really represent the average of growth in the open field Those corresponding to the two last experiments have been reared in artificially favourable conditions and cannot be considered as representing a mean of what occurs in natural surroundings

Further analysis of the data reveals that the second period is decisive any deficiency or excess of water in this period is reflected, more or less strongly, in the weight of the yield

As regards the first period, excessive moisture at this time is very harmful, to the extent of leaving the plants permanently injured and unable to seed In contrast, lack of water in this period should not be harmful, provided that during the second period it is compensated by a sufficient abundance In the third period the plants are less affected by the degree of moisture in the soil, since growth is now in a downward phase

We see, however, that the ratio between kilograms of water evaporated and of dry matter formed always tends to vary between 400 and 500, except under very abnormal conditions According to the above, if the mean results of the first experiment are accepted, the figures shown in *Table II* are obtained from their corresponding values

This can be adapted into a scheme of irrigation by using the volumes of water per hectare corresponding to the ratios given in *Table II* For one hectare this scheme would be as shown in *Table III*

We do not claim to have reached a definite conclusion by means of these data At the moment the experiments are being repeated in lisimeters as well as in trial plots at the Irrigation Estate of the National Institute of Agricultural Investigation After some two or three years' work it will no doubt be possible to confirm or modify these preliminary conclusions

Table III Irrigation Scheme for One Hectare

First watering	Preparation for sowing	900 m³
Second ”	30 days later	800 ”
Third ”	7 ” ”	700 ”
Fourth ”	7 ” ”	700 ”
Fifth ”	7 ” ”	700 ”
Sixth ”	9 ” ”	700 ”
Seventh ”	12 ” ”	600 ”
Eighth ”	15 ” ”	500 ”
Ninth ”	15 ” ”	400 ”
	Total	6,000 m³

OTHER ASPECTS OF RESEARCH WITH LISIMETERS

The influence of different soil types on the consumption of irrigation water and its requirements per hectare is well known and varies with the water capacity of the soil Again, the ratio between dry matter formed and water transpired varies with the composition of the soil and the fertilizing agents present These variables are also taken into account, and in the experiments with the more important crops a few lisimeters are set aside in which the type of soil is varied At the same time other lisimeters contain manure different from that used in the general experiments *i e* certain lisimeters are taken from the equilibrated humidity experiment so that the formula of the fertilizer in them can be varied

Fertilizers influence the quality of the harvest as much as does water supply, and for this reason the same type of experiment has been started, so far only with wheat, to investigate the bread-making qualities of different flours in relation to the supply of water and fertilizer The first advance in this field has already been published in two parts[2, 3] The results for one year only are recorded, but those for two other years will be published shortly

SUMMARY

Most regions of Spain have low rainfall and high temperature during spring and summer Thus the cultivation of irrigated crops becomes extraordinarily interesting, but water supply is limited and must be carefully controlled and utilized so as to derive the greatest possible benefit from it It is therefore necessary to know as accurately as possible the amounts of water which will be best suited to the needs of each crop in the various regions With this end in view a network of lisimetric stations has been created These determine by gravimetric methods the water requirements of each crop In this article the mechanism and function of the stations are explained, and some results given

REFERENCES

[1] CAVANILLAS, L *Bol Inst Invest Exp agron, for, Madr.* 9 (1949) 20
[2] — *An Inst. Esp Edaph. Ecol Fisiol veg* 7 (1948)
[3] SILVELA, F *Bol Inst Invest Exp agron for, Madr* 8 (1948)

Miscellaneous Notes

CHEMICAL RESEARCH LABORATORY

Industrial bacteria— Bacteria are used in all kinds of industrial processes from the production of yoghourt to the manufacture of solvents In order to provide industry and research laboratories with the cultures they need a national collection of industrial bacteria was begun at the Chemical Research Laboratory of the D S I R early in the year It took over the non-pathogenic cultures held by the National Collection of Type Cultures at Colindale and now houses some three hundred and fifty types This number is expected to be increased considerably as the Collection becomes more representative of the needs of industry

The Laboratory will maintain any organism which has ceased to be of interest but which may be wanted later It frequently happens that a particular organism is destroyed when it has fulfilled its temporary purpose and yet may be required in the future at short notice The Laboratory will also maintain any organism which for one reason or another should be duplicated Cultures may change character at an inconvenient moment, for instance, and this could hold up important work

Most of the non-pathogenic bacteria supplied up to now by Colindale can be obtained from the Chemical Research Laboratory and the Laboratory will try to procure any type of non-pathogenic culture which it does not hold itself In time, it is hoped that the collection will become comprehensive and gaps are being filled by obtaining cultures from other laboratories in this country and abroad Particular emphasis will be given to assay organisms

Cultures held by the Collection will be included in the *United Kingdom List of Species* to be published in 1951

BRITISH IRON AND STEEL RESEARCH ASSOCIATION

Low alloy steel standards for spectrographic and photometric analysis— Eight standards representative of the low alloy steel range are now available for routine and research spectrographic analysis The increased use of spectrographic analysis during and since the 1939–45 war led, through its sub-committee on Spectrographic Analysis, the Methods of Analysis committee of the B I S R A to put the provision of standards high on its programme Work on the subject began late in 1946, and recommended compositions for two series of low alloy steels and residuals were drawn up The manufacture, physical preparation and preliminary analyses of the low alloy series have been undertaken under the supervision of the Bureau of Analysed Samples Ltd

The eight standards are available in the form of 0 5 in (1 3 cm) diam rod, and are intended to cover a range of up to 5 per cent of the more usual alloying elements in steel, the iron content of each standard being 94 5 per cent approximately Analytical standardization has been carried out on behalf of the Methods of Analysis committee by twelve cooperating chemists in industrial, Government and research laboratories including the Bureau The percentage chemical analyses are as follows, tabulated in ascending order of each constituent

Silicon	0 01	0 13	0·18	0 25	0 29	0 37	0 62	0 81
Manganese	0 02	0 17	0 36	0 53	0 79	1 11	1 21	1 42
Nickel	0 05	0 18	0 56	0 84	2 08	2 92	4 10	5 15
Chromium	0 04	0 20	0 35	0 53	0 96	1 72	2 34	3 07
Molybdenum	0 01	0 19	0 32	0 43	0 54	0 95	1 29	1 41
Vanadium	0 03	0 12	0 22	0 26	0 36	0 48	0 52	0 65
Copper	0 09	0 11	0 11	0 18	0 23	0 24	0 31	0 50

The steels are also available in the form of fine turnings as standards for photometric methods of analysis (as an alternative to standardization by means of pure metals) The turnings for photometric standardization are supplied in a series of eight bottles, each containing either 100, 50 or 25 gm

BRITISH INTERNAL COMBUSTION ENGINE RESEARCH ASSOCIATION

At the Annual General Meeting held on 28 June the Rt Hon the Viscount FALMOUTH, M I MECH E, COMP I E E, was re-elected President of the Association for 1950–51

Lieutenant-General Sir FREDERICK G WRISBERG, K B E, C B, Dr S F DORBY, C B E, F R S, Air Commodore F R BANKS, C B, O B E, Sir LYNDEN MACASSEY, K B E, K C and Major-General CLAYTON, C B, C B E, were re-elected Vice-Presidents The Engineer-in-Chief of the Fleet, Vice-Admiral (E) the Hon D C MAXWELL, C B, C B E, was also elected a Vice-President

J JONES, M I MECH E, was re-elected Chairman of Council

COMING EVENTS

International Congress of History of Science, Amsterdam, 14–21 August

18th International Congress of Physiology, Zoofysiologisk Laboratorium, Copenhagen, 15–18 August

5th International Congress of Microbiology, Rio de Janeiro, 17–24 August

Annual Meeting of British Association for Advancement of Science, Birmingham, 30 August–6 September

International Mathematical Congress, Cambridge, Mass, 30 August–6 September

International Congress of Cell Biology, New Haven, Conn, 4–8 September

New Books

Techniques in Experimental Electronics

C H BACHMAN

(vii+252 pp, illus, 8½ in by 5½ in)

New York . John Wiley and Sons, Inc , 1948 $3 50
London Chapman and Hall Ltd, 1948 28s net

In the title of this book the word 'Electronics' has a meaning agreed by the American Standards Association *viz* 'That branch of science and technology which relates to the conduction of electricity through gases and *in vacuo*' The reader should therefore not expect to find in this book any treatment of electronic circuit techniques , but he will find a wealth of information on vacuum technique for both glass and metal systems, mechanical and diffusion pumps, methods of handling gases in low pressure systems and electrode and thermionic cathode construction, to mention only a few of the varied techniques described

The weakest section of this book is that dealing with the techniques associated with low pressure gas discharge work For example, there is very meagre information on methods of purifying gases and on the important problem of 'clean-up' There is a somewhat brief but useful section on the latest methods of leak detection and a very good account of modern techniques of evaporation and sputtering of metals

The reviewer was somewhat disturbed by the use, even under quotation marks, of the word 'bombard' to describe the induction or 'eddy current' heating of metals in vacuum apparatus

This book can be recommended to anyone embarking on a programme of research in which he requires up to date information on vacuum tube technique including the techniques associated with beams of charged particles It goes considerably further than the usual small books on vacuum work

J Sayers

Radio-Frequency Heating

L HARTSHORN

(237 pp, illus, 13 tables, 8½ in by 5½ in)

London George Allen and Unwin Ltd, 1949 21s net

Industrial High Frequency Electric Power

E MAY

(xi+355 pp, illus, 8½ in by 5½ in)

London Chapman and Hall Ltd, 1949 32s net

These, the first two books published in this country on the subject of dielectric heating, are fortunately complementary rather than similar Dr Hartshorn deals mainly with aspects of interest to the user, rather than 'detail required by the manufacturer of equipment' Mr May on the other hand presents an omnibus volume , 50 pp of elementary AC circuit theory lead to 110 pp of design of HF alternators and valve oscillators, while the subject of high frequency heating occupies only one third of the book There is a substantial chapter on HF measurements, whereas Dr Hartshorn refers for this aspect to his existing work on the subject Compression is the price of comprehensiveness, and Mr May devotes to induction and dielectric heating the same space as Dr Hartshorn does to each separately The disproportion is marked in the second subject, which Mr May dismisses in 24 pages It may be doubted whether so wide a range is really advisable, unless in a textbook primarily for student use

Dr Hartshorn, after a brief chapter on valve oscillators, divides his book into four roughly equal sections on induction heating and dielectric heating, each subdivided (unlike Mr May's work) into 'Principles' and 'Applications' In particular, the section on applications of dielectric heating (50 pp) is a valuable account of methods probably less familiar to engineers than the longer established methods of induction heating

The laboratory worker, already knowing the elementary theory and interested mainly in methods, will probably prefer Dr Hartshorn's account The student acquiring a general knowledge of the subject from scratch will perhaps prefer the inclusiveness of the other The designer of equipment and the works engineer will be well advised to acquire both, despite the inevitable overlap

Some omissions in either book arise from their differing plans Thus Dr Hartshorn, ignoring details of design, says almost nothing on the practically important subject of screening, while Mr May deals only cursorily with the whole subject of energy losses in dielectrics There are however a few notable omissions from both books Little is said concerning suitable insulation for the difficult conditions in apparatus where frequency, voltage and temperature are all high 'Breakdown' does not appear in either index, and although 'Electric strength' appears in Mr May's, 'field strength' is actually meant. The question of thermal stability, which determines whether a dielectric will or will not ultimately reach a stable temperature in a given electric field, is not mentioned, neither is the possible use of 'ferrite' materials for flux concentration which was demonstrated about three years ago, The reviewer has detected no errors of consequence Dr Hartshorn (p 55) takes the conductivity of tap water in ohm cm to be in microhm cm, so that his penetration depths for water should be multiplied by 1,000 Mr May gives formulae for the inductance of various conductor arrangements, without a warning that some of these are correct at low frequencies only His *Table 3* lists 'Phenol' (carbolic acid) where 'Phenol-formaldehyde resin' is intended His printer's happy invention of 'electron-motive-force' (p 1) suggests admirable foresight by the originator of the term EMF

C G GARTON

Technology of Plastics

B L DAVIES

(*xii+421 pp, 106 illus, 8½ in by 5½ in*)

London Sir Isaac Pitman and Sons, Ltd, 1949 37*s* 6*d* net

ACCORDING to the preface 'this book is intended for the use of students in technical colleges and others desiring a broad knowledge of plastic materials' With such a purpose in view, the subject has been dealt with in a general way under the main headings of thermoplastics, thermosetting resins, other plastics and other aspects of manufacture

In writing the work, knowledge of manufacture, structure and practical design including chemical, physical and engineering aspects has been required, and it is becoming increasingly difficult for a single author to survey accurately such a field The manuscript had been read by several colleagues and this has undoubtedly strengthened the technological sections, which are well described, but the polymer chemistry, which has been included with each of the individual plastics, has been insufficiently checked For example when dealing with cellulose the consideration given to FISCHER's obsolete formula is not justified, whilst there is no mention of the Haworth school for their development of the modern glucopyranose formula Representation of the linking of glucose residues to form the cellulose chain needs revising, since it ignores cellobiose, which is the intermediate structural unit In the paragraph on acetate moulding powder there is no justification for the comparison of the viscosity of the acetate employed with that used for rayon, or for the reference to the influence of viscosity on the cost of the powder The paragraph on p 82 on the connection between solubility and degree of etherification of cellulose is very loosely phrased, and on p 125 it is stated that polyethylene is 'believed to have a simple molecular structure of straight chains' of CH_2 radicals, whereas the existence of branches has been established

In view of the space devoted to bitumens, pitches and rubbers, which are not usually considered to be plastics, the absence of a chapter on plasticizers is noteworthy The book would also benefit by a chapter comparing and contrasting the individual types of plastics, and there are not even any tables of properties

The printing is good and the style used gives easy readability The descriptions of technological processes are assisted by the many diagrams and plant illustrations

There is nothing original in this addition to the general literature on plastics, and its price is likely to discourage students However, it is a useful summary and is recommended for those outside the polymer and plastics field requiring an overall picture of the industry

C DIAMOND

Atoms in Action

G R HARRISON

(*x+410 pp, illus, 8½ in by 5½ in*)

London George Allen and Unwin Ltd, 1949 12*s* 6*d* net

THIS book deals in a most imaginative and stimulating way with the impact of physics upon society, and covers a great deal of ground The author is a physicist and teacher, and his special field is spectrum photometry and spectrum analysis It is not surprising therefore that one of the best chapters in the book discusses a territory of which the author has first hand knowledge, the chapter entitled 'Eyes that see through atoms'

Not the least attractive feature of the book is the clear and personal style, and the frequent phrases of quiet humour Consider merely the following statement on p 225 'If cows did not like mustard there would be no motion picture industry' The Brains Trust might like to ponder a bit over this and a few other truisms which the book contains

It must be said, however, that the chapter 'When physics goes farming' is not quite so well balanced as some of the others The author seems to think that the main problems of farming, apart from soil fertility, are problems of physics since they involve investigations of temperature control, light intensity, soil mechanics *etc* That physics can help agriculture is true—principally perhaps by providing biologists with new tools with which to solve problems Any agricultural crop is an experiment in large scale plant physiology and we do not gain anything by even a faint suggestion that physics can do much more than provide new techniques

There is a story on p 33 about a rancher who used a high power incandescent lamp suspended above a tray filled with kerosene covered water in the centre of a sixty acre field, and by this means not only captured twenty gallons of insects in the first four nights of operation but also claimed that the light protected his beans, corn and tomatoes, and entirely eliminated the need for sprays and poisons. I think that if the author had consulted a few first class entomologists he would have omitted this story Personally I do not believe it I am also quite aghast at the statement on p 35 'The physicist is able to aid the plant physiologist and the geneticist in the rapid development of new species'

The customary spelling used in the United States has been preserved in the text, though not in the index May we in future have one or the other, please ? Nevertheless, apart from these minor points, this is a good book and should be read by all who believe that a knowledge of science is a part of our cultural heritage

S C Harland

Supersonic Flow and Shock Waves

R COURANT and K O FRIEDRICHS

(*xvi + 464 pp, illus, 9 in by 6 in*)

New York Interscience Publishers Inc 1948 $7 00
London Interscience Publishers Ltd, 1948 56s

Phenomena involving the propagation of violent disturbances have in recent years attained considerable prominence in engineering physics Detonation waves and blast waves are of this kind, similar phenomena occur in connection with the propagation of a shock in an elastic-plastic medium and also in hydraulics, but the subject has achieved its greatest measure of publicity in connection with the problems of transonic and supersonic flight For such disturbances the classical linear theory of wave propagation may cease to be a good approximation, and a non-linear theory supervenes This theory forms the subject of the book under review Its authors are interested primarily in the general mathematical and physical features of the theory and in the form under which these appear in the various fields mentioned above Thus the book is concerned throughout with the fundamentals of shock waves rather than with detailed applications to technical examples A clear distinction is drawn between basic physical assumptions and mathematical deductions

The book opens with two chapters on the fundamental properties of the physical medium, with particular reference to fluids, and on the mathematical theory of hyperbolic partial differential equations including the theory of characteristics Problems of one dimensional flow, of plane flow, and of flow in three dimensions, are then dealt with in succession. There is a separate chapter on flow in nozzles and jets The relative sizes of the spaces allotted in a book of this kind to the various subjects naturally depends on the personal interests of the authors, but it appears to the reviewer that a more detailed discussion of wave propagation in an elastic-plastic medium would have been appropriate The space allocated to the theory of detonation waves is disproportionate by comparison On a point of detail, the terminology regarding conditions of energy transfer in the theory of compressible fluids is not as yet standardized, and it is doubtful whether the use of the words 'isentropic' and 'adiabatic' suggested by the authors (p 5) will find general acceptance At any rate the reader should note the particular definitions adopted

The book is excellently written and can be highly recommended not only to the theoretical research worker but also to the development scientist who wishes to acquire a detailed knowledge of a subject which is becoming increasingly important for modern engineering

A Robinson

La Biologie des Sols

J DUCHÉ

(*128 pp, illus, 7 in by 4½ in*)

Paris Presses Universitaires de France, 1950 *c Fr* 90 00

This book is divided into three main sections the first deals with the organisms that live in the soil, the second with their interactions, and the third with the biological evolution of soils The matter is very much condensed in an effort to force it into the scope of 125 pages, but it is clearly presented, and there are only minor inaccuracies

It is inevitable that some subjects should have suffered more than others from lack of space, and in general the micro-flora and fauna are given preferential treatment, while earthworms and insects are dismissed in less than three pages Having enumerated the groups of organisms that are to be found in soil the author goes on to discuss their behaviour He first considers the interactions and associations of the different groups with each other, then their effect on the physical structure of the soil, and on its mineral and organic constituents

The figures given are for the most part poor, and the book suffers from the lack of references to original sources , the bibliography contains only six entries, and, apart from a list of chapters, there is no index.

L. M. Crump

Analytical Chemistry and Chemical Analysis, 1948

Proceedings of the International Congress on Analytical Chemistry, Utrecht, 1948

(*x+417-854 pp, illus, 9½ in by 6¼ in*)

Amsterdam and New York Elsevier Publishing Co Inc, 1949 $3 50

London Cleaver-Hume Press Ltd, 1949 27*s* 6*d*

Free to subscribers to Analytica Chimica Acta

THIS book is a reprint of an issue of *Analytica Chimica Acta* Vol 2 (1948) devoted to the International Congress on Analytical Chemistry organized under the auspices of the Netherlands Chemical Society and held at Utrecht on 1-3 June 1948

A short preface introduces the number and includes the names of the organizing committee and some facts about the meeting Then follows the report of the opening session giving the address by the President of the Congress, C J VAN NIEUWENBURG (Delft) on 'Analytical chemistry and chemical analysis, now and in the near future' and an address by G CHARLOT (Paris) on 'Le rôle actuel de l'ingénieur-analyste'

The bulk of the book consists of the proceedings of four of the five sections into which the Congress was divided, namely general methods and standardization (11 papers), electrical methods (11), optical measurements and physical methods of separation (13), and microbiological methods and detection of traces (10) The papers on emission spectrography have been published separately in *Spectrochimica Acta* The volume concludes with the address by P E WENGER (Geneva) at the final session summarizing the work of the Congress

The activities of the different sections cover a wide field of analytical chemistry and the lectures and papers range in scope from general surveys of modern developments, for example, in polarographic analysis (J HEYROVSKY, Prague) and chromatography (T I WILLIAMS, London) to accounts of original work on specialized procedures such as the use of *Aspergillus niger* for the determination of plant nutrients in the soil (F C GERRETSEN, Groningen) In general, emphasis is placed on physicochemical and physical techniques which, in modern analysis, are rapidly replacing or supplementing classical methods based on gravimetric and volumetric procedures

About three quarters of the total number of papers are in English including a large contribution from Dutch chemists and physicists The remainder are in French, from French and Belgian contributors Short summaries in English, French and German are included in many of the papers and notes of any subsequent discussion are appended

The reprint is bound in a stiff paper cover and provides in convenient form a valuable record of the activities of the meeting

P J HARDWICK

Monomers, I

Edited by F R BLOUT, W P HOHENSTEIN and H MARK

(*viii+340 pp, 9½ in by 6¼ in*)

New York Interscience Publishers Inc, 1949 $7 50

London Interscience Publishers Ltd, 1949 60*s*

THIS book consists of a series of monographs on various substances used in preparing polymers of industrial significance The scope of this first issue is indicated by the following headings Acrylonitrile (I WAITCHER, 37 pp), Butadiene (S POLSTEIN, 45 pp), Isobutylene (P SPITNIK, 32 pp), Isoprene (P SPITNIK, 37 pp), Methyl methacrylate (R S CORLEY, 36 pp), Styrene (S POLSTEIN, 63 pp), Vinyl acetate (P FRAM, 55 pp), Vinyl chloride (H SHALIT, 32 pp) The contributions are bound in a loose leaf cover, the intention being to add other sections from time to time

Each compound is dealt with under the common headings of introduction, production, purification and analysis, care and handling, physical properties, chemical reactions, polymerization and bibliography Apparently the intention has not been to produce a comprehensive dossier but to present new information and data likely to be of interest to those dealing with polymerization Nevertheless, references to early work *e g* TILDEN's on isoprene in 1897, are by no means excluded As would be expected, there is some unevenness of presentation but all the monographs have value For ascertaining rapidly a particular property of a monomer, or in finding a reference to a preparative method, the book is excellent It is doubtful however, whether it can be used so satisfactorily as a detailed source of information on laboratory methods At times, as for instance on p 4 of Isobutylene, descriptions of processes are obscure and the investigator will need to consult the original literature Furthermore, the proof reading, particularly of chemical formulae, is not satisfactory Such statements, also, as that on p 29 of Vinyl chloride, that a copolymer of vinyl chloride and vinyl acetate 'has high dielectric properties and, unlike polyvinyl chloride, it can be plasticized', are surprising in a work of this type

The idea behind the compilation is good so long as it does not lead to neglect of original papers The book provides a convenient source of data not readily available and includes a series of bibliographies having obvious interest Used critically, it will be of value to many investigators in the polymer field

N J L MEGSON

An Introduction to Molecular Spectra

R C JOHNSON

(xiv+312 pp, 159 illus, 8¾ in by 5½ in)

London Methuen and Co Ltd, 1949 40s net

THIS book is written for graduates or students nearing graduation and gives a comprehensive account of molecular spectra About two thirds of the volume is devoted to diatomic molecules , the remainder to polyatomic molecules, infra-red and Raman spectra, and to applications to astrophysics, chemistry, biology *etc* The emphasis is on the practical interpretation of spectra rather than on the pure theory of molecular structure No knowledge of wave mechanics or group theory is assumed, although their results are occasionally used

The book is well proportioned and although a very large amount of material is quite fully discussed the author has succeeded in presenting it clearly and avoiding giving any impression of overcrowding The volume is not unfortunately entirely free from errors , *e g* pp 25–26 there is a nasty confusion between Λ-doubling and spin splitting in $^2\Sigma$ states , on p 22 there are some queer ideas on the fluorescence of oxygen The part on diatomic spectra appears to be about ten years out of date , this is less serious than it sounds as the theory has advanced little in this time, but many examples are out-dated and some numerical results are now known to be in error The part on polyatomic molecules appears to be more recent, but is still hardly ' hot news '

In many sections the treatment is more complete and better than in other books on molecular spectra The discussions on the vibrational structure of diatomic band systems, on rotational intensity factors, and on the determination of effective rotational temperatures are particularly good On the whole the book is to be heartily welcomed, and it is to be hoped that a revised and up to date second edition will soon be called for

A G GAYDON

The Coming Age of Wood

E GLESINGER

(xv + 279 pp, illus, 8 in by 5½ in)

London Martin Secker and Warburg Ltd in association with Sigma Books Ltd, 1950 12s 6d net

IN a foreword by Sir JOHN (now Lord) BOYD ORR this book is stated to have been written, not for a few specialists but for the general public, in order to show the contribution which modern technology applied to forest products can make, both to industrial prosperity and to the increase of the world's real wealth The author is, at present, head of the forest products branch of the Food and Agriculture Organization of the United Nations, but the views expressed in the book are personal and not an expression of the views and policies of F A O By training Dr GLESINGER is not a wood technologist but an economist with a wood background He deals but lightly with the technical aspects of the many processes to which he alludes

The book is composed of three parts, in the first of which the theme is developed that wood will become ' the characteristic raw material of our civilization ' The familiar story of the dire results of uncontrolled exploitation of certain of the world's forests is unfolded and policies of conservation and integrated utilization are advocated This section includes a summary of the author's views about the importance of wood in world politics taken from his earlier book *Nazis in the Woodpile* Part II of *The Coming Age of Wood* is devoted to a series of highly simplified coloured diagrams prepared for the author by H BILLINGS to illustrate various phases of wood utilization

In Part III the author passes from the political to the technical and under such chapter headings as Cellulose, the Noble Molecule ', ' Lignin, the Enigmatic Key to Wood Chemistry ', and ' Wood Alloys ', gives a highly popularized account of such subjects as wood hydrolysis, pulp and paper manufacture, lignocellulose plastics, fibreboards, improved wood and wood distillation This is done in order to show that wood chemistry has an important part to play in securing complete and integrated utilization of wood This section of the book reveals that a knowledge of chemistry is, unfortunately, not included among Dr Glesinger's accomplishments

Nevertheless there is cause for careful husbandry of the world's forest resources and a very strong case for finding the best ways of using them The author has had opportunity far surpassing that of others for assimilating the facts relating to forestry and forest products The general reader may well wonder, however, whether the true interpretation of these facts is as simple as the author suggests

W G CAMPBELL

Books to Come

The Littoral Fauna of Great Britain, *Second edition* N B EALES (*904 pp, 25 illus, 8 in by 5½ in*) Cambridge University Press 20s net

New Atoms O HAHN New York Elsevier Publishing Co Inc

Funktionentheorie (2 vols) C CARATHÉODORY (*each c 220 pp, c 90 illus*) Basel Verlag Birkhäuser *c S Fr* 30 00 each

RESEARCH SUPPLEMENT

Some Kinematic Properties of Munroe Jets

W M EVANS, M Sc, Ph D. and A R UBBELOHDE, M A, D Sc.

In the early stages of the investigation only comparatively simple experimental means were available for determining the energy characteristics of Munroe jets Development of the physical concepts described elsewhere gave rise to certain test procedures for determining effectiveness of explosives*

ENERGY OF MUNROE JETS

Measurements of crater volumes after various distances of travel— Observations were made on the craters as the charge was moved away from the target Increased distance caused the depth of the crater to alter, owing to changes in the jet as it travelled through space (see *Figures 2, 5* and *6* in reference *) Detailed analysis of these changes of depth of 'penetration' was not possible until considerable theoretical work had been done, and will not be discussed here The volume of the crater also changed with increasing stand-off (*Figure 1*) At some distance from the base of the charge there was a catastrophic break-up or 'spattering' of the jet, the effect of which led to irregular craters (*Figure 2*) and was very strongly reminiscent of the break-up of a jet of water at some distance from the nozzle of a hosepipe Experiments showed that if the metal linings were shaped with careful attention to rotational symmetry, the distance the jet would travel before spattering was much greater than if deliberate asymmetries were introduced

Measurements of jet velocities— Whereas crater volumes gave an indirect measure of the total energy of the jets, measurements of jet velocity gave only the instant of arrival of the head of the jet at various points in space From the fragment evidence and other considerations it seemed likely that there would be a velocity gradient along most Munroe jets, so that they would extend in length as they travelled forward

Measurements on jet velocities were first made by timing the instants of closure of gaps in electrical circuits effected by the head of the jet as it travelled forwards No evidence of any acceleration of the head of the jet could be observed within a distance of two charge diameters from the base of the hollow For the shallow hollows comparative figures are given in *Table I*

The massive jets moved more slowly, as might be expected on dynamic grounds At any distance from the base of the charge the data fit the equation

$$MV^{2} = \text{constant}$$

where M is the mean mass of the lining and V the mean velocity of the head of the jet The decelerations of the various jets, fit approximately a formula of the usual type

$$\mathrm{d}V/\mathrm{d}t = kV^{n}$$

typical values being

$$\text{Unlined hollow } \mathrm{d}V/\mathrm{d}t = 2\ 4\ V^{1}$$

for detonation gases only and

$$\text{Steel lining } \mathrm{d}V/\mathrm{d}t = 0\ 088\ V^{2}$$

For the tin lining this simple relationship was not found to hold To a rough approximation the decelerations were found to be between one fifth and one seventh of the corresponding values for jets of the same velocities from unlined hollows

The very rapid decelerations observed for the unlined hollow charges explains their poor effects when placed some distance from the target This effect

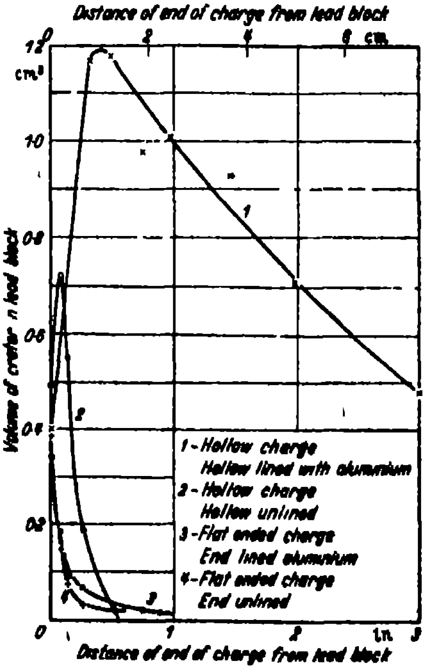

Figure 1 Axial damaging effects in lead blocks of small charges with shaped ends, as measured by volume of crater

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* EVANS, W M and UBBELOHDE, A R *Research* 3 (1950) 331

Figure 2 Appearance of steel targets due to 'spatter' or 'splash' of jets a 80° steel cone lining (top ½ truncated), thickness 0 027D, stand-off 5·5D, b 80° cadmium cone lining, thickness 0 044D, stand-off 6 5D

may be attributed to the very low densities of jets formed merely from the gaseous products of detonation of the explosive, compared with the densities of jets formed from hollows lined with metal

Measurement of jet energies by target calorimetry— By using a steel target as its own calorimeter, and specially protecting the thermocouples, it was possible to measure the total heat evolved by impact of a jet on the target leading to crater formation Experiments were limited in number but they showed that as much as 10 per cent of the total heat of detonation of the explosive charge might be liberated in the target due to jet action

LAWS OF PENETRATION AND OF SCALING

If d is the depth of penetration and D_e the calibre of the projectile in inches, then for a shell penetrating armour plate the relationship is of the well known form

$$D_e\, d^n = c E$$

where E is the kinetic energy of the projectile, and n is an exponent lying between 1 6 and 2, c is a constant depending on the type of armour plate

For fragments from a fragment gun the penetration is a function of the momentum per unit area i e

$$D_e^2\, d = c'p$$

where p is the momentum of the projectile and c' is a constant depending on the target material.

From a logarithmic plot (*Figure 3*) of the entry diameter against d the depth of penetration for jets from shallow spherical cap hollows, it was found that for steel linings of varying thicknesses and for thin copper linings the results could be expressed by a single formula, even near to the charge, namely

$$D_e^{2\cdot 3}\, d = \text{constant}$$

On the other hand all the points for the metals of low boiling point could be expressed by a single equation

$$D_e d = \text{constant}$$

These formulae break down very near the charge where jet formation is not complete, and far out where there is a falling off in penetration due to the effect of air resistance on the jet

The fact that general empirical formulae are found is of considerable interest, and probably means that a constant dynamic quantity was imparted to the

Table I Velocities of Various Munroe Jets (Shallow Hollows)

Distance from base of charge D	Velocity (ft/sec*)				
	Lining Thin steel (mean wt 5·63 gm)	Thick steel (mean wt 6·64 gm)	Thin tin (mean wt 5·68 gm)	Thick tin (mean wt 7 01 gm)	Unlined
3	9,600	—	14,100	10,800	22,600
4	9,600	—	13,950	10,100	21,700
6	9,500	—	13,800	9,800	18,900
8	9,400	7,000	13,100	8,500	15,400
10	8,250	6,900	12,500	9,100	13,000
12	8,100	6,800	11,900	8,600	10,850
14	8,050	6,700	11,150	8,100	8,100
16	8,000	6,600	10,400	7,600	7,600

* 1 ft = 0·305 m

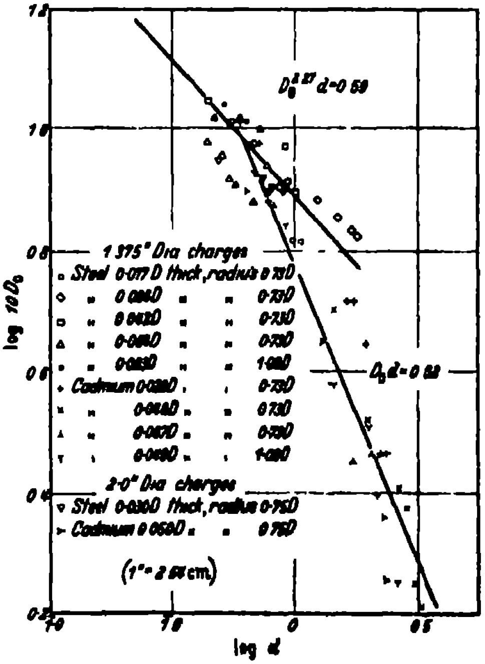

Figure 3 Laws of penetration and scale effects in steel penetrated by jets from charges with various spherical linings

metal The velocity measurements on the jets indicate that this constant quantity is kinetic energy

Charges scaled linearly obeyed the same empirical formulae when lengths were expressed in units of charge diameter.

Jets from the deeper lined hollows such as hemispheres and cones gave results which could not be fitted to the same empirical equations, indicating the possibility of a different mechanism of jet production and of target penetration

EXPERIMENTAL DETAILS AND RESULTS

Jet velocities— For the detection of the passage of the head of the jet with time, gaps were formed by fine strips of metal about 1 mm apart and placed at intervals of from 1 to 2 in (2 5 to 5 0 cm) in the direction of travel of the jet The closures were recorded on an Argon lamp chronograph reading to 1 microsecond From the space/time plots the space/velocity curves could be constructed

Target calorimetry— This involved setting up steel targets on strong supports with small areas of contact, so as to minimize loss of heat by conduction A thermocouple was inserted axially upwards from the bottom of the target, to a depth determined by previous experiments, so that the disturbance of the target metal at the bottom of the crater, when this was formed by the jet, just failed to break the couple It was important to have the couple as near to the crater as possible to secure temperature/time curves which required the minimum extrapolation After the shot had been fired, the temperature first rose to a peak, then the temperature/time curve flattened as the heat was re-distributed in the steel, and finally it fell uniformly due to heat losses from the steel to the ambient air Rather rough methods of approximation had to be used to allow for these losses, but as the rise of temperature was around 15C° the order of magnitude of the heat liberated in the target could be estimated with fair accuracy

Penetration laws— Simple calibration methods were used to measure the depth and entry diameter of the craters formed for various distances between the charges and the target

In studying the effect of charge dimensions it was assumed that the unit of length was the diameter of the explosive filling So far as supplies of metal tubing and metal linings permitted, all the other dimensions were increased *pro rata* to the diameter of the explosive charge Theoretically it need not follow, for explosive phenomena, that all the dimensions scale linearly, but so far as the penetration data over the range of diameters 1 to 1½ to 2 in (2 5 to 5 0 cm) were concerned linear scaling of results was observed within the experimental error

Acknowledgements are due to the late Sir Robert Robertson, K B E , F R S , for his interest and encouragement throughout the course of these investigations and to the Chief Scientist of the Ministry of Supply for permission to publish this account of them The photographs are Crown copyright and are reproduced by permission of the Controller H M S O

Armaments Research Establishment
Ministry of Supply

(*Received May 1950*)

A Mathematical Typewriter

J R GREEN, D Phil , B E and G H HARRIS

The difficulty of producing mathematical reports in typescript is frequently encountered It has been solved in one particular laboratory by constructing two typewriters of standard make as one interconnected unit Since the number of symbols available is doubled, such typewriters can be used not only for mathematical work but also for foreign language glossaries and dictionaries and for biological papers where italics are constantly used A description of the mechanism is given

EARLY in the 1939–45 war, when the Aeronautical Research Laboratories, Department of Supply and Development, Melbourne, Australia, were established, the need to reproduce mathematical reports arose No special mathematical typewriters were available locally, while the import from U S A of a *Vari-Typer* was subject to great risk It was decided to use a modification of an available typewriter

The standard type of machine in use in the Laboratories had interchangeable keyboards so a spare keyboard specially fitted with Greek letters and mathematical symbols was adopted However, it involved typing a complete page on the normal keyboard, leaving spaces for mathematical symbols, then substituting the special keyboard in order to go over the page again to fill in the mathematics This was not only slow, but required careful judgement, concentration, and experience to produce a pleasing and balanced result Though for more than four years all reports were typed in this way, some

Figure 1 Front view of the assembled typewriter

improvement in apparatus was clearly needed. It was finally decided to build a double typewriter to obviate the changing of the keyboard and doubling back over the work. One desirable feature was the automatic setting of the carriage so that it would be in the correct position to type the next letter after transfer from one keyboard to the other. It was clear that there were many mechanical solutions to this problem, but the one adopted was simple and suggested itself when the standard components were examined prior to commencing construction. The automatic indexing system for tabulating found in this make of typewriter provided the basis.

Our experience has been favourable enough to warrant others constructing a similar machine for typing mathematical or other reports needing more characters than those found on a standard typewriter, but which do not justify the expense associated with the great flexibility of operation of the *Van-Typer*.

DETAILS OF CONSTRUCTION

Two standard *Imperial* typewriters are used. These have interchangeable keyboards, though this is not a necessary refinement. The carcasses are bolted into an angle iron frame and adjusted at exactly the same height. The centre distance is an exact number of letter spacings, the carcasses being about 0·1 in (0·25 cm) apart. *Figure 1* shows the front view of the machine.

Keyboards— The left hand keyboard has Roman characters. The right hand keyboard was specially fitted with mathematical symbols, Greek letters and small figures for subscripts. The symbols are shown in *Figure 3*, the new arrangement was the result of much thought and trial, and provided the opportunity to eliminate the difficulties found in the original mathematical keyboard. The type was obtained from the makers of the typewriter and fitted by the local agents to a standard keyboard. The tabular keys and back spacers of the two typewriters are mechanically linked, the former by a torsion rod and the latter by levers. These links are clearly seen in *Figure 2* for the preparation of which the carriage was removed.

Escapement mechanism— The plunger on the left hand machine is operated by an electromagnet which presses on the back of the escapement mechanism. This can be seen in *Figure 2*. It operates on 10 v DC supplied by a rectifier. The traversing motion of the carriage is controlled by the escapement mechanism of the left hand machine, the right hand mechanism being removed as can be seen in *Figure 2*. An alteration was made to the plunger of the right hand machine to enable it to enter a small knife switch. It was found that a microswitch was unsuitable. The rapid bouncing action of the keys did not give sufficient time of contact to operate the magnet.

Carriage— The original carriages were removed and a standard 26 in (66 cm) carriage was fastened to the left hand carcass; it just sits on the machined faces of the right hand carcass (see *Figure 2*). As noted already, the machines are adjusted to exactly the same height. The rubber roller was found to be unsuitable and was replaced by a cork roller.

Transfer mechanism— The margin adjuster was removed and replaced by a slider carrying locating fingers to pick up the index plates, the effective length of the slider being equal to the distance between the typewriters. This is shown in *Figure 4*.

When the carriage is moved into the right hand position the near side of the left hand finger on the slide comes up against a stop and the far side finger on the right end of the slide engages with one of the index plates. The reverse takes place on the left hand side.

The action of this slider and the stops fixed to the machine immediately below the tabulated setting mechanism (*Figure 4*) is the same as that of two stops fixed to the frame on either side of the setting mechanism at a distance equal to the distance

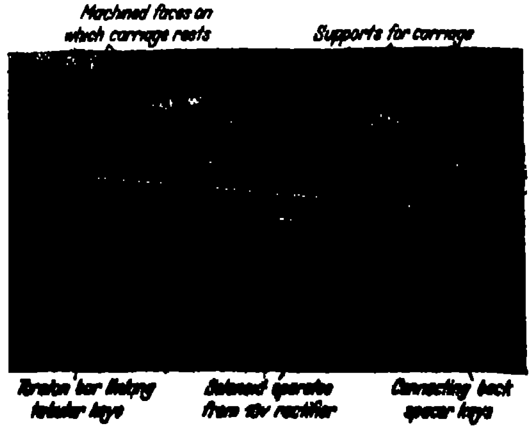
Machined faces on which carriage rests
Supports for carriage
Torsion bar linking tabular keys
Solenoid operated from 10v rectifier
Connecting back spacer keys

Figure 2 Twin carcasses with carriage removed

First row	√	π	<	>	≈	∂	∞	∇	∫	ϑ	Λ	§
	1	2	3		5	6	7		9	0	λ	∠
Second row	Θ	α	—	{	→	=	[	–	Ω	×	Γ	
	ϑ	β	γ	}	t	y	]	.	ω	p	ϰ	
Third row	Ξ	τ	ν	ε	χ	ι	σ	Φ	∝	Ψ	Δ	
	d	ϱ	μ	ξ	η	ζ	Σ	φ	l	ψ	δ	
Fourth row	}	~	'''	≡	Π	∫	+	|	{	(	)	
		z	x	c	v		n	m				

Figure 3 Symbols and Greek letters on the right hand keyboard of the mathematical typewriter

between the two machines The provision of two fixed stops would have necessitated a modification of the end frames of the moving carriage to avoid fouling and one of the stops would have had to be overhung rather a long way from the carcasses of the typewriters so that it seemed simpler to use the internal stops and slider

To move the carriage from one keyboard to the other the typist merely pulls down the control bar shown in *Figure 1* and, holding the bar in the 'down' position, moves the carriage in the desired direction until it comes to rest against a stop as outlined above The carriage is now in the correct position to continue typing and the bar is restored to the 'up' position The detailed sequence of events is as follows

As the control bar is pulled towards the operator, a pin *C* forming an extension of the normal automatic tabulator setting bar is carried upwards by a pawl *A* thereby setting an index plate of the tabulating mechanism (*Figure 5*) The arcs of travel of the pin and pawl are adjusted in the design so that when the pin reaches the end of its normal travel the pawl slips out of engagement with it and the control bar is free to continue its movement As the control bar is pulled further down, an inclined face on its end lever engages a small roller attached to the lever which lifts the rack out of engagement with the pinion on the escapement mechanism The carriage may now be moved along until it is arrested by the appropriate stops The control bar is now restored to the 'up' position During the first part of this upward motion the rack is lowered into engagement with the pinion, the pawl being free to deflect so that the pin remains undisturbed in its uppermost position A projection *B* now engages the pin so that completion of the upward movement of the control bar restores the pin to its initial position and removes the index plate from the path of the fingers on the slider Typing can now proceed using the new keyboard

Figure 4 Showing slider and other accessories

Tabulation—It will be clear from the preceding description that tabulation can be done on either keyboard by moving the control bar full down to throw a stop and back half way The index plates are then not wiped out but remain at the tabulating position They can be cleared by moving the bar right up

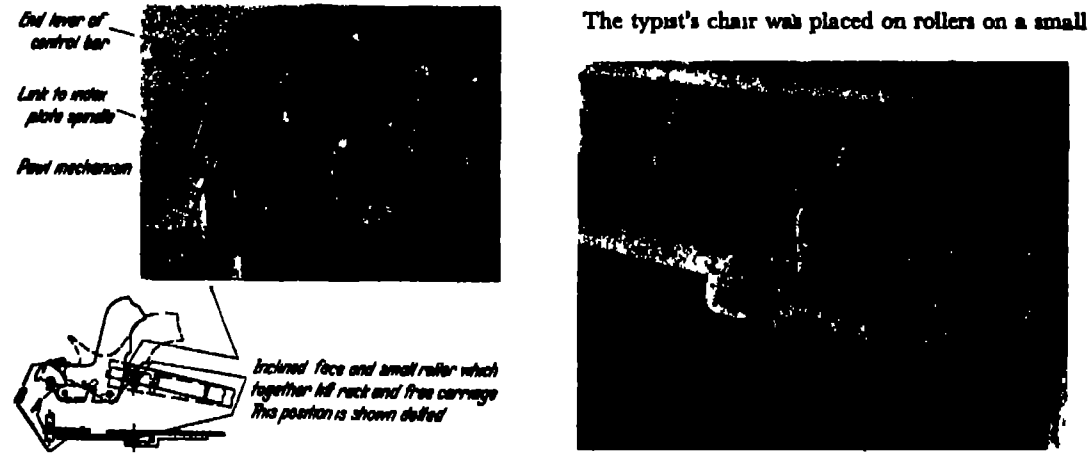
End lever of control bar
Link to motor plate spindle
Pawl mechanism
Inclined face and small roller which together lift rack and free carriage This position is shown dotted

Figure 5 Transfer mechanism details left, end view, right, rear view

Miscellaneous— As the margin stop was removed to fit the transfer slider, another stop had to be attached, as shown in *Figure 4*, to be engaged by the line spacer A projection on the end of a torsion rod is turned to engage this stop when the line spacer is pulled over This stop is fixed and the paper must be correctly placed in the machine to give the right width of margin

The line spacer had to be lengthened because of the extra length of the machine

The typist's chair was placed on rollers on a small track so that it could slide to one side or the other and be in front of the keyboard in use

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(*Received April 1950*)

Research Correspondence

Effect of Temperature on Lateral Spacing of Fatty Acid Monolayers on Metals—an Electron Diffraction Study by Transmission

SEVERAL workers have investigated the effect of temperature on the structure of thin films of long chain carbon compounds on metal surfaces using the electron diffraction reflection method

Since this method is not suitable for determining changes in the lateral spacing of the hydrocarbon chains a technique for examining films by transmission has been developed. The specimen, mounted on a disk of 200 mesh/inch (79 mesh/cm) silver gauze, is clamped firmly between two cylindrical silver blocks which constitute the specimen holder The electron beam passes through an axial hole in the blocks The specimen is heated by passing a current through a heating coil surrounding the holder A thermocouple consisting of fine platinum and silver wires is attached to the specimen holder and is calibrated by observing the melting of small crystals of organic compounds of known melting point deposited on the gauze

The temperatures recorded by the thermocouple represent the true temperature of the specimen to within 5C° A fuller description of the holder is given elsewhere[1]

Some preliminary experiments have been carried out with fatty acids deposited on cadmium A piece of cadmium foil 1 5 cm × 1 5 cm × 0 002 cm was degreased and a layer of the fatty acid deposited by the rubbing technique described elsewhere[2]. Examination of this layer by reflection confirmed that a well oriented film had been prepared. The foil was then floated with the fatty acid layer uppermost on a N/1 ammonium nitrate solution which rapidly attacked the underside of the foil. When judged sufficiently thin it was removed on a silver gauze and transferred to a water surface for washing. A suitable piece of the foil was picked up on a specimen grid and placed in a desiccator to dry.

Examination in the camera revealed a pattern comprising rings from cadmium, cadmium oxide and hydroxide together with a rather diffuse halo of spacing about 4·1 Å from the acid layer. Experiments were made with stearic ($C_{17}H_{35}COOH$), m pt 69°C, and octacosanoic acid ($C_{27}H_{55}COOH$), m pt 90°C.

The simplest hypothesis to explain the appearance of the pattern is that, at room temperature, the layer consists of small aggregates of molecules with the hydrocarbon chains approximately normal to the surface, the planes of the chains being randomly distributed in azimuth. The closest packing of the chains in such a system would be such that there is a chain at each point of a hexagonal lattice. If the diffuse halo arises from the (110) spacing of this array then we can calculate[3] an area per chain equal to $a^2\sqrt{3}/2$, where $a = 2d/\sqrt{3}$ and d is the spacing of the (110) ring. We find for octacosanoic acid a value of 18·4 ± 0·4 Å² and for stearic acid 19·0 ± 0·4 Å², for the rubbed layers at room temperature. This is somewhat less than the value of 20·0 Å² given by HAVINGA and DE WAEL[4] for Langmuir-Blodgett layers of polar compounds, but is in close agreement with the x-ray data for the acid in bulk.

Reflection experiments show that oriented layers of fatty acids on metals, when heated, become disoriented at a characteristic transition temperature[2, 5, 6]. The transition temperature on reactive metals is near the bulk softening point of the metallic soap formed by reaction between the acid and substrate. In the present experiments the surface film disorients at about 120°C and therefore probably consists of the appropriate cadmium soap. It is found that the Bragg spacing corresponding to the halo increases with temperature and at the transition temperature is approximately 4·45 Å. Assuming that the hexagonal structure is still present although much more disordered on account of the thermal motion of the molecules, this corresponds to an area per chain of approximately 23 Å². The spacing is close to the value of 4·6 Å reported by STEWART and MORROW[7] for similar liquid hydrocarbon compounds. Thus the mean distance between the molecules in the surface film after disorientation is not markedly different from that of the molecules in the bulk liquid.

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(*Received June 1950*)

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The Hydrogenase of Azotobacter

THE discovery that the hydrogenase of Azotobacter is an adaptive enzyme formed during the uptake of gaseous nitrogen, and not during the uptake of fixed nitrogen even in the presence of gaseous hydrogen, has indicated a close relationship between the hydrogenase and nitrogenase systems of Azotobacter[1]. This indication is supported by the competitive inhibition by hydrogen of nitrogen fixation by Azotobacter[2]. Recent investigations on nitrogen fixation by anaerobic Clostridia and photobacteria have given further evidence on the suggested relationship between the two enzyme systems. The rate of nitrogen fixation by *Clostridium pasteurianum* is unaffected by gaseous hydrogen, although the total nitrogen fixed is somewhat depressed[3]. This difference between Azotobacter and the Clostridia may be due to an adaptation of the latter to the hydrogen evolved in its own metabolism. The bacterium *Rhodospirillum rubrum* has been shown to be capable of fixing nitrogen under conditions that permit photoproduction of hydrogen[4, 5]. The significant discovery was also made, that the photoproduction of hydrogen by *R. rubrum* is inhibited by gaseous nitrogen on certain substrates[4]. The possibility of a relationship between hydrogenase and nitrogenase led LINDSTROM, BURRIS and WILSON to test for nitrogenase activity certain organisms known to possess a hydrogenase.

Positive results were obtained in two cases[5]. The great physiological differences between the various groups of nitrogen-fixing organisms suggest that the relationships between the various hydrogenase and nitrogenase systems vary with the organism. The symbiotic nitrogen fixing system, in particular, has no concomitant hydrogenase activity[6]. The characteristics of some hydrogenases have been studied. The responses of the Azotobacter hydrogenase to inhibitors and variations in pH_2* have been measured[7, 8], and show similarities to the hydrogenase of *Proteus vulgaris*[9]. **Wilson** and **Burris** have suggested a unifying mechanism, involving hydrogenase, for nitrogen fixation in Azotobacter, postulating free radical reactions[10]. It was suggested that the free radicals could arise from a reversal of the hydrogenase reaction. The reversibility of the hydrogenase was assumed, by analogy with that of *P vulgaris*. The reversibility of the Azotobacter enzyme has become of great interest following the report by **Rittenberg** (footnote to ref 4) that resting suspensions of *R rubrum* in the dark do not catalyse the exchange reaction between deuterium oxide and hydrogen, unlike the hydrogenase of *P vulgaris*.

The reversibility of the Azotobacter hydrogenase has been investigated here in connection with attempts to simulate nitrogen fixation *in vitro*. It has been shown that the Azotobacter enzyme is reversible, thus bearing out the assumption of **Wilson** and **Burris**. This result may point to a significant difference between the systems in Azotobacter and Rhodospirillum. A previous attempt to prove the reversibility of Azotobacter hydrogenase was inconclusive[11]. The method adopted here was to enclose a deuterium-oxygen atmosphere over a suspension of incubated *Azotobacter vinelandii* in a nitrogen-free mannitol medium, and to analyse the residual gas for the presence of the light hydrogen isotope after suitable intervals. Under these conditions, the Knallgas reaction can proceed in an effectively resting suspension. Since only a qualitative result was required, a simpler apparatus was used than that necessary to study the Knallgas reaction under optimum conditions. 3 × 10^{10} cells from a pure culture were freshly suspended in 20 ml of medium and placed in a 100 ml bulb, and after evacuation the flask was refilled with a mixture of 90 per cent deuterium and 10 per cent oxygen. The bulb was incubated at 40°C and periodically shaken. Samples were withdrawn at intervals and dried by passage through a spiral liquid air trap. Deuterium samples were prepared by sparking the gas mixture at a low pressure in a glass chamber set between two liquid air traps. The apparatus was kept free from grease to avoid any hydrogen production during sparking. Deuterium analyses were made by means of a thermal conductivity gauge having an accuracy of one per cent in analysing deuterium-hydrogen mixtures. Three samples of the deuterium-oxygen atmosphere were tested *a* before admission to the bulb, *b* 15 minutes after admission and *c* 60 hours after admission. The analyses of the residual deuterium were respectively *a* 99% D_2, 1% H_2, *b* 99.5% D_2, 0.5% H_2, *c* 90.8% D_2, 9.2% H_2. Analysis *c* proves the evolution of hydrogen, and hence the reversibility of the hydrogenase. All possible impurities in the gas preparations (*e g* nitrogen) have lower thermal conductivities than deuterium, so that the appearance of hydrogen is unequivocal. A report on the free radical experiments will be published elsewhere.

We wish to thank Dr J H Singleton for the deuterium analyses

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* Here pH_2 denotes the hydrogen pressure

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Frictional Properties of Porous Metals Containing Molybdenum Disulphide

Molybdenum disulphide is an interesting material from the frictional point of view. It is analogous to graphite in that it possesses a laminar structure and gives a low coefficient of friction. It also has the advantage of being stable up to high temperatures. If a thin film of molybdenum disulphide is rubbed on to steel surfaces, the coefficient of friction at low speeds of sliding is reduced from $\mu = 0.8$ to $\mu = 0.05$. The film adheres to the metal reasonably well but on repeated sliding it is worn away and the friction rises. Some account of the frictional behaviour of molybdenum disulphide at high speeds of sliding has been given by **Johnson**, **Swikert** and **Bisson**[1].

The experiment has been tried of incorporating the molybdenum disulphide in a porous metal

Various metals have been used, but the behaviour of molybdenum disulphide in sintered copper is shown in *Table I.*

Table I Steel Slider Load 4 kg

Substance	*Coefficient of friction*	
	Initial	*After repeated sliding*
Solid copper	*c* 1 3	*c* 1 3
Sintered copper	*c* 0 3	*c* 0 8
Sintered copper containing molybdenum disulphide	0 15	0 13

Variation of Coefficient of Friction with Temperature

Temperature °C	15	100	200	300	400
Solid copper	1 3	1 3	*c* 1 0	*c* 1 0	*c* 1 0
Sintered copper	0 3	0 7	0 8	1 2	1 2
Sintered copper containing molybdenum disulphide	0 13	0 14	0 13	0 14	0 2

It will be seen that the copper containing molybdenum disulphide gives a small coefficient of friction which remains at a low value after repeated sliding ($\mu = 0\ 13$). Even at comparatively high temperatures the friction is still low (at 300°C $\mu = 0\ 14$) At 400°C the coefficient of friction has risen to $\mu = 0\ 2$ but this is probably due mainly to excessive oxidation of the copper

In a second series of experiments sintered molybdenum was used and the molybdenum disulphide was formed chemically *in situ*.

The results are shown in *Table II*

Table II. Steel on Molybdenum Load 4 kg

Substance	*Coefficient of friction*	
	Initial	*After repeated sliding*
Sintered molybdenum	0 4	0 45
Sintered molybdenum containing molybdenum disulphide	0 1	0 1

Variation of Coefficient of Friction with Temperature

Temperature °C	15	100	200	300	400
Sintered molybdenum	0 45	0 5	0 5	0 5	0 55
Sintered molybdenum containing molybdenum disulphide	0 1	0 08	0 06	0 06	0 07

The molybdenum containing molybdenum disulphide gives a lower friction than sintered copper under similar conditions because the sintered molybdenum is harder and the area of contact between it and the slider is correspondingly reduced It will be seen that the coefficient of friction may be as low as $\mu = 0\ 07$ even at 400°C. This is lower than that observed at room temperature with well lubricated metals The sliding process will continue to feed a thin film of molybdenum disulphide on to the surface so that the friction remains low after prolonged rubbing and the general behaviour is similar to that of a porous metal impregnated with a low friction plastic[2]

Experiments showed that the wear and surface damage of steel sliding on pure molybdenum was heavy on the treated molybdenum it was very slight.

Thanks are due to Murex Ltd for preparing the molybdenum

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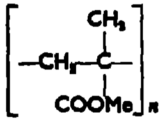
Frictional Behaviour of Plastics Impregnated with Molybdenum Disulphide

The frictional behaviour of some plastics[1] and of a porous metal impregnated with plastic[2] has been described earlier With some plastics the coefficient of friction is high For example, with steel sliding on *Perspex*



$$\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOMe}{C}}- \right]_n$$

the coefficient of friction is $\mu = 0\ 45$

Some experiments have been carried out with plastics containing a small amount of molybdenum disulphide In one series of experiments, *Perspex* was mixed with a few per cent of molybdenum disulphide and moulded in a press at 3,000 lb/in^2 (211 kg/cm^2) at 170°C Before each measurement the surface was cleaned by scraping with a diamond scraper so that a fresh surface was exposed The results are shown in *Table I*

Table I Steel Slider Load 4 kg

Substance	*Coefficient of friction*
Perspex	0 45
Perspex containing molybdenum disulphide	0 1 to 0 15

With repeated sliding the untreated plastic showed heavy surface damage and wear. With the plastic containing molybdenum disulphide the track formed was smooth and the friction remained at the low value ($\mu = 0{\cdot}15$).

In a second series of experiments the molybdenum disulphide was incorporated in a thermosetting plastic Approximately 1 per cent of molybdenum disulphide was stirred into a solution of ebonite in petrol and this was spread as a thin film on a metal surface and then baked The frictional behaviour is shown in *Table II* The slider here was copper

Table II Copper Slider Load 4 kg

Ebonite layer after repeated sliding	$\mu = 0\ 4$
Ebonite layer containing molybdenum disulphide	$\mu = 0\ 25$

The presence of small amounts of molybdenum disulphide did not appear to have any marked effect on the mechanical properties of the plastics The main effect was to lower the friction

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Index of Non-uniformity of Particle Shape

If surface s and volume v of individual particles in a sample of particulate matter have been determined by microscopic measurement *i e* calculated on the basis of the observed individual shape from the projected diameter, the expected value of the ratio s/v, in symbols $E(s/v)$, can be calculated as the arithmetic mean of all the ratios s/v Instead of calculating that expectation statistically we might, by experimental methods, be it permeability, light extinction, adsorption methods *etc*, determine the specific surface of the sample of powder, as

$$S_v = \frac{a_s \Sigma d_i^2 n_i}{a_v \Sigma d_i^3 n_i} = \frac{E(s)}{E(v)}$$

where d_i is the projected diameter, n_i is the number of particles of that size, and a_s, a_v are the surface and volume shape factors respectively

The two quantities, $E(s/v)$ and $E(s)/E(v)$ as the expectation of a ratio of two functions of d_i and the ratio of their expectations, are connected by the general inequality relation[1, 2]

$$\underline{|E(f/g) - E(f)/E(g)|} - K \leqslant \frac{\sigma_f}{\sigma_g} \qquad (1)$$

where f, g are arbitrary functions of one and the same variable, K is the greatest value of the ratio f/g, σ_f and σ_g are the respective standard deviations, and v_g is the coefficient of variation of g We have therefore

$$\frac{|E(s/v) - S_v|}{v_v^2} - K \leqslant \frac{\sigma_s}{\sigma_g} \qquad (2)$$

For particles of strictly uniform shape, the ratio s/v is constant no matter what the size of the particles and therefore

$$E(s/v) = E(s)/E(v)$$

On the other hand, the more the particles differ in shape, the greater will be the difference between the individual ratios s/v and, therefore, between the two members of the inequality which, thus, may serve as an index of non-uniformity

The quantity on the left expressed as a percentage of σ_s/σ_g could be used as an index number for non-uniformity The greater the percentage, the greater the non-uniformity

The realization of that inequality may lead to an important correction of the Kozeny equation for the permeability constant[3]

$$K = \frac{l_s/l_w p^3}{36(1-p)^2} d_w^2 = \frac{l_s/l_w p^3}{(1-p)^2 S_v^2} \qquad (3)$$

where l_s/l_w is a constant depending upon the shape of the capillaries in the bed of powder, p is the pore volume expressed as a percentage of the total volume, d_w is the volume-surface diameter and S_v is the specific surface per cm³

The differential equation which leads to the above formula is set up under the assumption that the infiltration in the soil in one capillary is inversely proportional to the square of the grain surface per cm³. For an aggregate of n grains, the average grain surface per cm³ is needed, that is the average of (grain surface/grain volume) Kozeny now takes as his model an aggregate of spheres, for which

$$E(s/v) = E(s)/E(v) = 6/d_w \qquad (4)$$

and substitutes this value into his equation.

But apart from the correction for non-sphericity of particle shape, the need for which is usually recognized, which would result in the numerator of the third member of equation 4 being greater than 6, $E(s/v)$ is, in general, not equal to $E(s)/E(v)$, unless the particles are strictly of one and the same shape, which is hardly ever so in a natural powder, and this correction has so far been overlooked. This may account for part of the unexplained systematic discrepancy in the specific surface if determined by permeability methods and calculated by Carman's modification of the Kozeny equation, on the one hand, and by adsorption methods, on the other[4]

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Some Effects of the Ultrasonic Irradiation of Deoxyribonucleic Acids

Recently we have been interested in isolating from bacterial sources various macromolecules and in particular deoxyribonucleic acid (DRNA)[1] In order to disrupt bacterial cells without using chemical reagents some workers[2, 3] have subjected them to ultrasonic vibrations Although this treatment is often effective, we have noted that the DRNA obtained from cells disrupted by this procedure gave aqueous solutions of a much lower viscosity than those isolated from similar cells disrupted in a mechanical shaker or in a bacterial mill Consequently it was considered of interest to investigate the action of ultrasonic irradiation on aqueous solutions of DRNA The DRNA used was prepared from *1* calf thymus gland by the method of Mirsky and Pollister[4] and deproteinized by the procedure due to Sevag[5], *2* soft herring roes by a slight modification of the Mirsky and Pollister[4] method and deproteinized by the method due to Hammarsten[6], and *3* wheat germ according to the method of Laland, Overend and Webb[7] The apparatus used for generation of the ultrasonic waves consisted of a valve oscillator with two *Osram MT16* valves in parallel, coupled to an *X*-cut quartz crystal The applied voltage was about 10 kv and the anode current *c* 70 ma At maximum output the total energy dissipated by the crystal was *c* 100 w, of which about 5 per cent was converted to sound energy On irradiating 0 2 per cent solutions of the nucleic acids, the viscosity decreased rapidly On standing, the solutions did not regain their original viscosity values, indeed it was observed that the viscosity continued to fall slightly, a phenomenon resembling that observed after x-irradiation of DRNA[8, 9] The ultrasonic irradiated samples always showed a *p*H value less than that of the original solution No ammonia could be detected in such irradiated solutions of DRNA from wheat germ or herring roe, but extended irradiation of solutions of DRNA from calf thymus gland resulted in some loss of the nitrogen present, in the form of ammonia (*cf* Greenstein *et alii*[9], and Scholes, Stein and Weiss[10]) Negligible amounts of inorganic phosphate were formed and the products from the irradiation were still relatively insoluble in acids The refractive indices of the native and corresponding irradiated samples in solution were identical as also were their ultraviolet absorption spectra, thus showing that no groups exhibiting strong absorption were liberated during the irradiation Solutions of the native and irradiated materials were dialysed in cellophane bags at 37°C for 4 hr against distilled water Negligible amounts of material of low molecular weight passed through the membrane Comparative measurements on diffusion rates using the simple apparatus of Gage[11] on native and irradiated samples showed no significant difference in diffusion rates, confirming the absence in the irradiated material of polynucleotides of low molecular weight This was further confirmed by the fact that both samples could be precipitated from solution by ethanol in the presence of sodium chloride Preliminary work with electron micrographs has indicated that whereas in the native DRNA long thin fibres can be observed, none is discernible in irradiated samples

The evidence presented indicates that some disaggregation of the samples of DRNA is induced by ultrasonic irradiation, but that the products are still of relatively high molecular weight Further proof of the disaggregated nature of the products of the irradiation was provided by an examination of some of their physical properties Unlike the native DRNA which showed structural (anomalous) viscosity in the viscometer due to Frampton[12], the irradiated products exhibited no anomalous behaviour Moreover in the simple apparatus of Edsall and Mehl[13] the irradiated products did not show the birefringence characteristic of the native material Electrometric titration data supported the view that ultrasonic vibrations disaggregate DRNA[14] and indicated that some of the hydrogen bonds are broken Enzyme studies on the irradiated material further confirmed this observation For example we have shown that the action of ox pancreas deoxyribonuclease on DRNA results in an initial decrease in viscosity without the formation of acid-soluble polynucleotides[15]. When the irradiated samples of DRNA were incubated with this deoxyribonuclease under identical conditions at *p*H 7 0, no decrease in viscosity occurred while the formation of acid-soluble material commenced immediately It would appear that ultrasonic irradiation disaggregates DRNA to a less complex polynucleotide which is highly susceptible to attack by the nucleotidase It is apparent that when isolating such macromolecules from micro-organisms, ultrasonic vibrations for disrupting the cells should be avoided A full account of this work, which is being extended, will be published elsewhere

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Note on Diffraction by a Dislocation

Hall[1] has pointed out that a first approximation to the atomic displacement produced by an edge dislocation is given by an expression of the same form as that for a screw dislocation[2], the difference being that the displacement vector is perpendicular to the axis of the dislocation instead of parallel to it To Hall's approximation one may write for the displaced position of the *j*th unit cell

$$\bar{r}_j' = r_j + \frac{\psi}{2\pi} t \tag{1}$$

where

$$\bar{r}_j = j_1 a + j_2 b + j_3 c \tag{2}$$

The axes are chosen so that c is parallel to the axis of the dislocation, ψ is an angle measured from some fixed direction perpendicular to c, and t is the Burgers vector (If in the undislocated crystal a large closed circuit is described about the dislocation axis, t is the gap produced in it by the dislocation It is necessarily a lattice translation) It may be shown that the reciprocal-lattice representation of diffraction by a cylindrical crystal of radius A containing an axial dislocation with displacements given by equation 1 is very similar to that previously described[2] for a screw dislocation The regions of high intensity are again disks perpendicular to the dislocation axis , they increase in diameter with increasing $S_0\, t$, where $\bar{S}_0$ is the vector joining the centre of the disk to the centre of the reciprocal lattice In the special case of a screw dislocation t is parallel to c, so that this is a generalization of the increase with l previously found

The amplitude of diffraction of x-rays is

$$\begin{aligned} G &= F\Sigma_j \exp\{2\pi i S\; r_j'\} \\ &= F\Sigma_j \exp\{2\pi i\bar{S}\; r_j + iS\; t\psi\} \end{aligned} \tag{3}$$

As previously shown, the summation over j_3 can be performed immediately, and verifies the statement that the regions of high intensity are disks perpendicular to the dislocation axis With $S = S_0 + \varrho$, where $\bar{S}_0$ is a reciprocal-lattice vector and ϱ is small compared with the reciprocal axes, the factor in the amplitude involving ϱ can be put in the form

$$G'(\bar{\varrho}) = \int_0^A \int_0^{2\pi} \exp\{2\pi i\varrho r\cos(\psi - \theta) + i\bar{S}\; t\psi\} r\,dr\,d\psi \tag{4}$$

where the sums over j_1 and j_2 have been replaced by integration over the cross section of the crystal, and r,ψ , ϱ,θ are the components of r and ϱ perpendicular to c expressed in polar coordinates Since t is a lattice translation, $\bar{S}_0\; \bar{t}$ is an integer, say p, and $S\; t$ differs from p by a small quantity $\bar{\varrho}\; t$ If this is ignored, which is legitimate in the immediate neighbourhood of the points of the reciprocal lattice, equation 4 becomes

$$G'(\varrho,\theta) = 2\pi i^p \exp\{ip\theta\} \int_0^A J_p(2\pi\varrho r) r\,dr \tag{5}$$

This differs from the corresponding factor for a screw dislocation only through the substitution of the integer p for the integer nl, and through the phase factor exp $\{ip\theta\}$, which has no effect on the intensity of diffraction To the extent to which Hall's approximation and the neglect of ϱ t are legitimate, therefore, the results obtained for a screw dislocation may be used generally with the substitution of p for nl

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Crystal Structures of l-Ephedrine Hydrochloride and Hydrobromide

The unit cell dimensions and space groups of the isomorphous *l*-ephedrine hydrochloride and hydrobromide were determined by Gossner and Neff [Gossner, B and Neff, H *Z Kristallogr* 86 (1933) 32] They found

	a	b	c	β	Z	*Space group*
l-ephedrine HCl	12 64	6 15	7 34 Å	102°6	2	$P2_1$
l-ephedrine HBr	12 74	6 20	7 62 Å	100°48′	2	$P2_1$

The structures of these compounds have now been examined in detail Patterson syntheses were used to find the positions of the chlorine and bromine atoms in the unit cells, and signs of the structure factors in the centric [010] zones were calculated directly from the relation

$$F_{\mathrm{HBr}}(h0l) - F_{\mathrm{HCl}}(h0l) = 2f_{\mathrm{Br}} \cos 2\pi(hx_{\mathrm{Br}} + lz_{\mathrm{Br}}) - 2f_{\mathrm{Cl}} \cos 2\pi(hx_{\mathrm{Cl}} + lz_{\mathrm{Cl}})$$

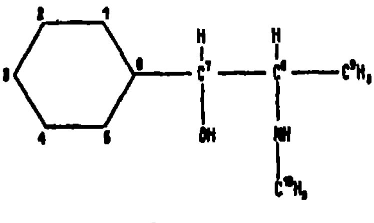

Figure 1 Structural formula of ephedrine The carbon atoms are numbered to correspond with Figure 2

The electron density map of the [010] projection was plotted for *l*-ephedrine hydrochloride by the use of these signs It showed the arrangement of atoms in the molecule, though some, particularly those in the benzene ring, were imperfectly resolved. The phases of structure factors in the acentric [001] zone were then calculated for a trial structure consistent with this [010] projection, and the ordinary methods of Fourier refinement have led to the electron density map shown in *Figure 2* Refinement is proceeding, the present values of the reliability index, $R \equiv \Sigma||F_o| - |F_c||/\Sigma|F_o|$, are $R[010] = 0\ 22$ and $R[001] = 0\ 19$

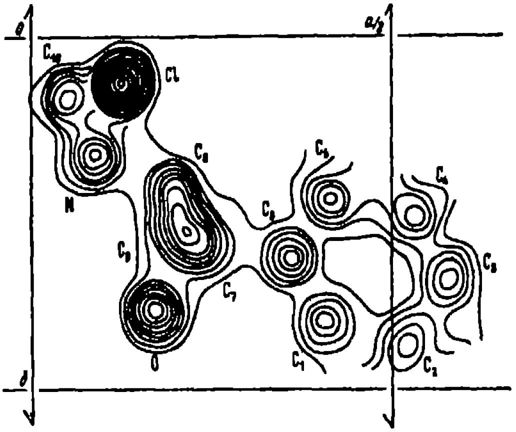

Figure 2 Electron density in l-ephedrine hydrochloride projected along the c axis [001] *The contour lines enclosing the chlorine atom are drawn at intervals of 2 electrons per Å² the remaining contours are drawn at intervals of 1 electron per Å² starting with the 2 electron line Only one molecule is shown*

Full details will be published elsewhere

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Commentary: Pleasure and Pursuit in Science

A GREAT DEAL MORE has been written about the purpose and social function of science than about the personal motives of the scientist. However, it is only by seeking to analyse the nature of the scientist's pleasure in his work that we can obtain clear ideas on what science is about. In the course of a presidential address to the Classical Association some years ago, Lord GREENE declared that science is one of the humanities. This remark is of great interest to the scientist, but its truth can be examined only by considering in the first place the quality of thought or feeling which accompanies scientific activity.

How are we to account for the intense interest and pleasure of science? It is a question which is by no means simple or straightforward. The work of the scientist is dispassionate to a high degree and for this reason it would appear to have little appeal to those instincts and emotions which psychologists believe to be the driving force of all effort and behaviour. That there is, however, a general quality of *feeling* in science, as there is in art or religion, is the main contention of the present article.

EINSTEIN himself has written 'Feeling and desire are the motive forces behind all human endeavour and human creation . . . .' He goes on to describe the nature of the cosmic religious emotion which accompanied and sustained the scientific work of men such as KEPLER and NEWTON who spent years of solitary labour in disentangling the principles of mechanics. 'Only those who realize the immense efforts and, above all, the devotion which pioneer work in theoretical science demands, can grasp the strength of the emotion out of which alone such work, remote as it is from the immediate realities of life, can issue.'

This lofty view is one which it is appropriate for EINSTEIN to express on behalf of other scientists of his period. However, before considering it in detail, it seems useful to examine the nature of scientific interest at several more superficial levels of emotional quality. For it must be admitted that the general run of scientific work, whether in pure or applied science, is concerned with rather restricted problems of immense detail, with the result that the cosmic emotion tends to become subordinated to feelings of a more everyday kind, although none the less entirely human in their quality.

In the following I shall try to analyse the motives of the scientist at three different levels of intensity. First in relation to the desire for adventure, the satisfaction of achievement and the pleasure of logical thought. Secondly, and very briefly, in relation to the aesthetic quality of science. Finally in relation to religion, returning thereby to the view expressed by EINSTEIN.

In developing this thesis it would be easy to overlook important alternatives, for the discussion of motives is always complex. It might be asserted, for example, that the scientist and engineer pursue their work because it is useful. It is, of course, for his value in society that the scientist deserves his pay, just as much as the miner or musician. However, what we are concerned with in this article is not so much the value of science to the community as the origin of the scientist's own personal enjoyment of his work It is certainly in the *doing* of research, rather than in its useful results, that we must find the origin of this pleasure and this, I believe, applies almost equally in both pure and applied science However, this is not to deny, in an age with a strong social conscience, that the usefulness of the work is an important incentive

DISCIPLINE AND ADVENTURE

To commence then at the most superficial or day to day level of scientific work, there is the enjoyment of intellectual effort, the satisfaction of curiosity and also, especially in experimental work, the sense of craftsmanship These matters are so obvious as to need little comment But they are sustained, I believe, by two factors which lie at a rather deeper level These are the satisfaction of disciplined thought and the desire for adventure

Now the process by which thoughts are generated in the mind is an utterly disorderly one (or so it seems) and bears no relation to the logical sequence of a scientific argument Let us suppose that at a particular moment our attention is centred on a certain object, say a clock On making a subsequent analysis of our mental or emotional processes we find that it is impossible to maintain our attention on the pure ' clockness ' of the clock, the thing in itself There is, in fact, nothing to think about in the clock as a pure thing Instead our minds slip spontaneously along a sequence of associations which begins with the clock and ends—anywhere These associations may have a predominantly emotional tinge or a predominantly intellectual one The images which rise in the mind may be due to the shape or colour of the clock, the sound of its tick or the word which denotes it Or we may slip along lines of thought such as our memory of the purchase of the clock or semi-scientific thoughts on its mechanism. In any case these thought trains very quickly leave the original object and pass elsewhere

Associative thinking of this sort is very enjoyable but it is not satisfying in itself, for it does not give rise to any sense of achievement It is a kind of thinking which has its important part in creative work, because it leads to the genesis of new ideas, but alone it does not give rise to a concrete and finished result The thought is satisfying and fruitful only when the conscious mind eventually imposes order on the meditative process It does this not by preventing the formation of spontaneous images but by imposing a limit to the thought trains Instead of running on indefinitely, as in day dreams, it seems as if the associative process is pulled up abruptly, every few seconds, for a general stock-taking and re-direction This process requires a distinct effort of will and, when the mind is fresh, we take definite pleasure in its orderly forward movement to the assigned objective, which is the solution of the problem in hand

To come then to our main point, it is evident that scientific subjects are particularly suitable for this controlled exercise of the mind This is partly because there is a clear objective which is desirable in itself, but also because the field of thought is *never exhausted* A train journey which is repeated each day becomes wearisome because it ceases to provide new stimulus The scientific journey is not of this kind , although it is an orderly one it is at the same time new and adventurous For in science we use the vast unknown of the universe as a constant source of fresh adventure for our thoughts

To summarize, we can say that scientific work satisfies simultaneously our need for orderly and disciplined intellectual effort and our desire for adventure There is an unlimited field of inquiry and therefore everlasting scope for new thought and new discovery

I am not speaking here in a journalistic sense, for major discoveries are, of course, very rare and fall to the lot of very few workers But in a proper sense all the work of a scientist, his reading and experiment, is a process of personal discovery, even though it may be of apparently quite small things Any well known chemical reaction carried out in a test tube is an act of re-discovery This is very clear from the fresh pleasure which we experience when we demonstrate to a child some of the historic experiments of science, such as PRIESTLEY's preparation of oxygen

AESTHETIC QUALITY OF SCIENCE

So much for the aspects of intellectual effort and adventure I shall consider only very briefly the aesthetic quality of science as one of the motives of research, for it has already been discussed in some detail by POINCARÉ, DIRAC and others This emotion is the pleasure of harmonious relations, but whether these relations are to be thought of as being constructed in man's own mind or as actually operating in external nature is an open question On the one hand, the point of view may be taken that the universe is quite unknowable but that the human mind is capable of constructing a theoretical edifice of great beauty and simplicity which serves to correlate the multiplicity of observational data Alternatively, and more simply, it can be said that Nature is a kind of living force which operates according to certain harmonious laws which can be discovered through science However, a philosophical question of this sort in no way affects the pleasure which is created by the discovery of comprehensive relations in natural phenomena What SHELLEY said of poetry might equally be said of science 'Poetry lifts the veil from the hidden beauty of the world and makes familiar objects be as if they were not familiar '

GEORGE SARTON has said that the history of science is to a certain extent a history of taste It is one of the faculties of the outstanding scientist that he is able to distinguish those theories which have qualities of harmony and elegance from those which have not Sarton continues 'One might ask "These theories that are more beautiful—are they more true ?" Anyhow, they are easier to grasp and more fertile , and for these reasons alone it is worth while to give them our preference '

From a certain point of view the aesthetic quality of science is most evident in the methods of theoretical physics, which is the most satisfying branch of science in regard to economy of hypothesis and logical consistency On the other hand it is in the applied sciences, such as engineering, that one appreciates most completely the extraordinary power and versatility of those laws which are established by physics, so that large machines can be accurately designed on the basis of a few generalizations due to NEWTON and CLAUSIUS Finally, it is in the more comparative fields of science, such as biology or inorganic and organic chemistry, that we depart from the beauty of simplicity and find aesthetic pleasure of a different kind in the wonderful variety and diversity of observed behaviour Thus each salt of each metal has its own special properties of colour, reactivity or the beauty of its crystalline form and structure

RELIGION IN SCIENCE

It seems probable, however, that science has certain springs of emotional or imaginative power at a still deeper level For it is certain that to a great number of men and women science has the compulsive quality which religion had in the middle ages We thus come finally to discuss the religious background of scientific feeling and for this purpose it is useful, in the first place, to consider the early history of science

There is a widely held view that modern science developed rather suddenly as something quite distinct from astrology and alchemy Such a view is not supported by history and is contrary to a great deal of general evidence that human thought is slow and evolutionary *i e* it moves forward mainly by the modification or improvement of ideas which already exist

It seems more correct, therefore, to regard science as having a fairly continuous history and it thus becomes permissible to examine the motives of the modern scientist in relation to the undoubted religious significance of early science, especially alchemy The motives which were the original driving force in science may be expected to be still active to some extent at the present time.

The earliest sources of science and religion were perhaps largely in the efforts of primitive man to achieve some degree of mastery and understanding of his environment The belief in nature as being activated by spirits was an attempt to obtain a causal understanding of natural phenomena by interpreting them in terms of the motives of unseen beings This was a scientific activity, and the use of magic and religious ritual which accompanied it may be regarded as a primitive technique of experiment which aimed at the control or placation of the unseen forces Science is thus the dangerous revealment of that which is secret, a source of power and knowledge It is a feeling which is by no means unknown at the present day Pierre Mabille has remarked ' Dans la découverte, quelle qu'elle soit, que ce soit science, art, amour, le combat d'homme est semblable, l'atmosphère dangéreuse identique Ce sont les mécanismes d'invention et de prophétie qui opèrent, ceux de la tradition d'évocation magique '

At a later stage the development of alchemy was closely linked to the intensely religious outlook of the middle ages A suggestive account of the psychological basis of alchemy has been given by Jung, who regards it as a religious activity based on the notion of redemption As the Saviour redeemed mankind, so man in his turn must purify and redeem inanimate matter In his search for the philosopher's stone the true alchemist was seeking not wealth but to effect a purification of the world at large.

This theory of the symbolic and religious character of alchemy is consistent with the theological emphasis of the middle ages and is supported by Jung by numerous quotations from the alchemists themselves For example, from Majer · ' . chemistry excites the artifex to meditation on the good things of Heaven, and that he who is initiated of God in these mysteries casts aside all such insignificant cares as food and clothing, and so appears to himself as if he were born anew'

In the middle ages the reality of the spirit seemed no doubt so clear that there was a strong tendency to interpret nature in terms of its symbols It was perhaps a continuation of the more primitive belief that natural phenomena were the work of unseen beings. However, as a result of various historic factors, such as the reformation and Cartesian philosophy, the power of symbolism declined and with it astrology and alchemy. Science entered into a prolonged period of mechanistic interpretation of nature which greatly increased its powers of analysis The resulting gain in the intellectual content of man's outlook was obtained at the expense of a diminution of the emotional content The development of science has enriched man's thoughts in many directions but in others it has impoverished it As Polanyi has said, certain kinds of meaning have been almost lost. One of the mainsprings of scientific activity remains, however, the attempt to interpret nature in terms of the human mind. The emotional basis of the urge to discovery is the projection into matter of the scientists' own spirit Thus from Jung ' . science began with the stars . Astrology is a primeval experience, and so is alchemy . . ' ' Everything unknown is filled by psychological projection , it is as if the investigator's own psychic depths were mirrored in the darkness ' However, many scientists find it necessary to believe, as an act of faith and a *raison d'être* of their work, that the logical relations which are discovered by science are not merely the projection of their own minds but are the mirror of an intelligibility actually existing in the external world Such a view undoubtedly gives a greater sense of purpose in science In this connection also there is a suggestion of Polanyi that the process of discovery is akin to the recognition of the shapes of things, as discussed in the Gestalt psychology In science the ' shapes ' we are concerned with are the interrelationships of natural phenomena ' All these processes of creative guesswork', says Polanyi, ' have in common that they are guided by the urge to make contact with a reality, which is felt to be there already to start with, waiting to be apprehended '

In its most intellectual form the ' cosmic emotion ' of the scientist is thus mainly related to the desire for reason in nature Philip Toynbee has remarked that humanity has an unconscious belief in order behind confusion

The success with which a great interlocking structure of relations can be built up gives a firm impression not only of the ability of the human mind to form adequate concepts of the universe but also of its intrinsic design It leads thus to a strong conviction of purpose and divinity There are two things, says PLATO, which lead men to believe in the Gods, one is knowledge about the soul, that is the most ancient and divine of all things, the other is our knowledge concerning the regularity of the motion of the stars and all other bodies under the dominion of the mind which ordered the universe

The emotional quality of science is thus in what it gives us of power and beauty and adventure, but more than anything in its revelation of orderliness This desire for reason in nature derives partly from a primitive need for confidence (for without order there can be no security) but in a much larger sense it is the expression of a religious outlook To the modern spirit it is science more than anything else which shows evidence of design and purpose in the external world It is moreover the clear and luminous intelligibility of science, rather than its actual content of knowledge or useful application, which is its most valuable contribution to human thought

There is another important incentive in science which is ethical rather than religious and is discussed very thoroughly by POLANYI This is the feeling of brotherhood The scientific community has certain common aims and ideals and this gives rise to a feeling of solidarity and dedication

It would, of course, be unwise to suggest that science, in its ethical content, is in any respect an alternative to organized religion, for it is, after all, very limited in its field of experience. At the same time it is perhaps the recognition that there are certain ideals in science which causes a great number of men and women to take it up as a career

Finally, to all scientists, whether their work is successful or not, there is in the doing of science a certain quiet detachment, a cool lake, as it were, on a hot day. This calm pleasure is well expressed by GOETHE 'I am going on, though slowly, with my papers on Natural Science, not because I think that I can materially advance science, but on account of the many pleasant associations I maintain by it Of all occupations, that with nature is the most innocent'

CONCLUSIONS

In summary, the origin of the pleasure of science has been considered under two rather different aspects Under the first it was suggested that the doing of scientific work is highly enjoyable in itself, because it is a progress of the mind along a route which is adventurous and is at the same time orderly and creative. Under the second it was proposed that there are certain emotional incentives in science, closely related to religious feeling. It is probably no accident that the devotion which was at one time created by theology is now largely inspired by science

In discussing these aspects of enjoyment in science it is, of course, not to be overlooked that the personal pleasure of the scientist is largely irrelevant to his purpose in society This arises from the fact that the appreciation of science for its own sake is mainly confined to the scientists themselves on account of the very extensive training which seems to be needed before this appreciation can be effective Thus whereas music is enjoyed by a great many, and literature and painting by a rather smaller number, the pleasure of science is restricted to a very small section of the community, so small, in fact, that the very large national expenditure on science could not be justified on this basis alone

The value of science to humanity at large thus lies in an entirely different direction to that of the arts — namely, in its useful applications to man's health and comfort, in its value as a technique of clear thought and investigation, and finally in the impression to which it leads of an orderly and intelligible universe These contributions are great enough but it may perhaps be hoped for the future that improved methods of exposition of science may lead also to its more extensive appreciation as a form of pleasure.

K. G. DENBIGH

Study of Imperfect Crystals by Powder Photographs

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X-RAY diffraction by crystals may be used for two purposes the study of crystal *structure*, and the study of crystal *texture* In structure determination the end sought is a knowledge of the positions of the atoms within the unit cell, the fundamental building block of the crystal, in texture study the aim is a knowledge of the perfection with which the unit cells are arranged H LIPSON[1] has described several examples of crystal structure determination, but mentioned only one texture problem There are, however, many of these, divided broadly into two classes In the first the crystal lattice is undistorted, and the size of the regions that diffract coherently is limited either by the crystal boundaries, *Figure 1*, or by 'mistakes' in the sequence of unit cells, *Figure 2* In the second class the crystal lattice is distorted and the size of the regions that diffract coherently is limited by displacement of the atoms from their ideal positions, *Figure 3* In the present paper the effect of texture on powder photographs is treated more systematically So far these have been most important in detailed texture study but they suffer from certain limitations[2], some of which are mentioned in the appropriate places

In taking a powder photograph, the specimen, a small rod consisting of many crystals, is placed at the centre of a cylindrical camera and irradiated by an approximately parallel and monochromatic beam of x-rays These are reflected at angles θ which are related to the wavelength λ of the x-rays and the interplanar spacings d of the crystals which make up the specimen by the Bragg law $\lambda = 2d\sin\theta$ When the film is developed the reflections appear as a series of lines For determining the interplanar spacings d, and thence the unit cell dimensions, the only significant property of a line is its position, from which θ can be calculated The lines, however, differ also in intensity and profile, as illustrated by the photometer curves, *Figure 4* The total intensity of the line, that is the area between the photometer curve and the interpolated background, depends on the kind and number of atoms within the unit cell but not on the crystal texture (The phenomenon of *extinction* is neglected It is not ordinarily of great importance in powder photography[3]) This so-called 'integrated intensity' is the quantity required for crystal structure determination The line profile, the distribution of intensity as a function of angle, depends critically on the crystal texture Usually only the breadth of the line is measured, though this is not a complete specification of the profile Two definitions of breadth, the half-breadth and the integral breadth, are in common use. The first is the width of the photometer curve, expressed in radians, measured at half the height of the peak The second is the integrated intensity of the reflection I divided by the peak intensity P These definitions obviously give quantities of the same order of magnitude, but may differ by 10 to 25 per cent The integral breadth has several advantages, and in what follows 'breadth' without qualification means 'integral breadth'

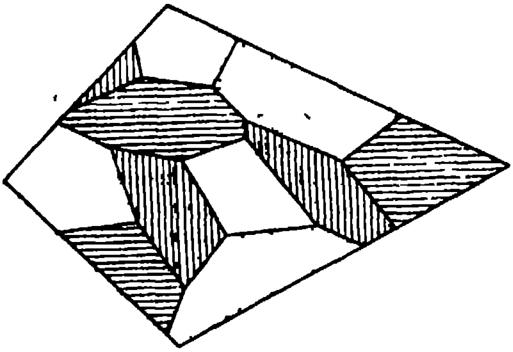


Figure 2 Crystal with mistakes In the domains with different shading the unit cells are alike in size and shape, but differ in the kind or arrangement of atoms within them For some at least of the reflections the regions that diffract coherently are smaller than the crystal

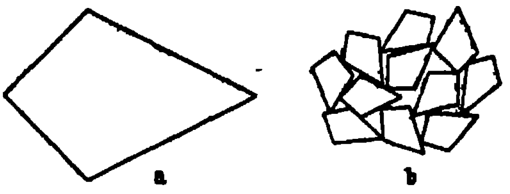


Figure 1 a *Large crystal All the cells composing it can diffract in phase* b *Aggregate of small crystals Only the cells within an individual grain diffract in phase*

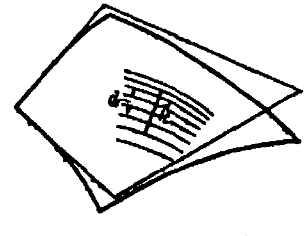


Figure 3 Distorted crystal The relative displacement of two planes a distance T apart is $\epsilon T + \frac{1}{2}\epsilon' T^2$ + where ϵ and ϵ' are the local values of the strain and strain gradient, they will no longer diffract coherently if this differs from ϵT by more than $\frac{1}{4}d$ The size T_c of the coherently diffracting regions is thus given by $\frac{1}{2}\epsilon' T_c^2 \sim \frac{1}{4}d$, $T_c \sim (d/\epsilon')^{\frac{1}{2}}$

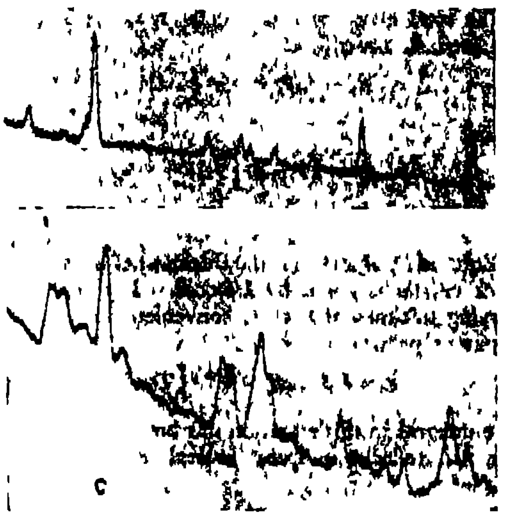


Figure 4 *Photometer curves* a *Portion of quartz pattern, showing sharp lines* b *Portion of china clay pattern, showing broad lines*

The breadth of a line as measured on the film is made up of three components *1* an intrinsic breadth β, a ratio depending only on the crystal texture, *2* a trigonometrical factor, $2\tan\theta$, the same for all varieties of texture, and *3* a broadening due to imperfections in the experimental arrangements Among the causes of this last broadening are inhomogeneity and lack of parallelism of the x-rays, and finite size of the specimen It may be eliminated by comparison of the photometer curves of lines from the specimen under investigation with those of lines from a 'perfect' specimen of similar size and absorption coefficient, although the calculations are tedious[4-7] (For this purpose a specimen made from ground quartz or an annealed wire of a pure metal may be regarded as perfect.) Geiger-Müller counter powder spectrometers can be designed with the instrumental broadening much less than is usual for powder cameras, and for this reason are preferable for texture studies, though their greater cost is a disadvantage

PARTICLE-SIZE BROADENING

A better understanding of the intrinsic breadth may be obtained, and the form of the trigonometrical factor may be verified, from a consideration of the simplest variety of broadening, that caused by small particle size In the usual derivation of the Bragg law the condition for a strong diffracted beam is obtained by considering the interference between rays scattered by successive planes of atoms in the crystal, *Figure 5*. Each successive plane of atoms reflects a small fraction of the beam of x-rays incident at the angle θ, ordinarily these interfere with one another and there is no strong resultant beam, but at one particular angle the path difference between successive beams is one wavelength and all the beams add together The condition for this to occur is that $PE + EQ = \lambda$, where P and Q are the feet of perpendiculars dropped from the point B where the ray ABC is reflected on to the ray DEF The lengths of PE and EQ are each $d\sin\theta$, so that this gives Bragg's law, $\lambda = 2d\sin\theta$, immediately[*] The peak intensity is proportional to n^2, the square of the number of layers, and the integrated intensity to n, so that we may define the ideal or intrinsic integral breadth by

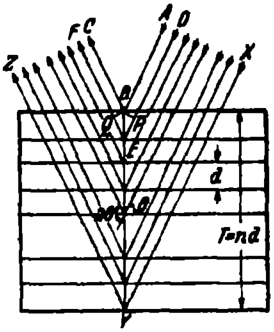
$$\beta_i = \frac{I_i}{P_i} = \frac{n}{n^2} = \frac{d}{T} \tag{1}$$

where I_i is the intrinsic integrated intensity and P_i is the intrinsic peak intensity

We have now to seek the relation between the intrinsic breadth so defined and the breadth β_f measured on the film and corrected for experimental imperfections When the crystal in *Figure 5* is reflecting most strongly, the ray XYZ reflected by the last plane travels a distance $2T\sin\theta = n\lambda$ farther than the ray ABC If the crystal is turned a little out of the reflecting position, say so that the angle of incidence of the x-rays is $\theta + \delta$, where δ is small and θ satisfies Bragg's law exactly, the extra distance travelled by the ray XYZ will be $2T\sin(\theta + \delta) - 2T\sin\theta$, or approximately $2\delta T\cos\theta$ If δ is such that this is one wavelength, the intensity of reflection will have fallen to zero, because for each ray reflected in the upper half of the crystal there will be another reflected in the lower half which is exactly out of phase with it The order of magnitude of the breadth of the reflection is therefore given by the value of 2δ which makes $2\delta T\cos\theta$ equal to λ, that is by

$$\beta_f = \frac{\lambda}{T\cos\theta} \tag{2}$$

Figure 5 *Derivation of Bragg's law and particle-size broadening*



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[*] Bragg's law is often written $n\lambda = 2d\sin\theta$, where n is the order of reflection. For the present purposes, however, it is more convenient to regard all reflections as first order, with spacings $d = d_0$, $d = d_0/2$, $d = d_0/3$ etc

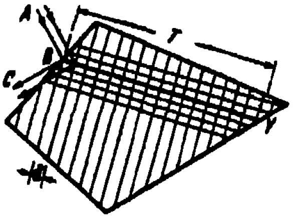

Figure 6 Calculation of the peak intensity of reflection from a crystal of varying thickness The crystal is divided into units each with volume equal to that of the unit cell and height equal to the spacing of the reflecting planes

The factor two (2δ instead of δ) comes in because the deviation of the x-rays in *Figure 5* is 2θ, so that the spread on the film is twice the spread in θ A calculation of the line profile shows that this estimate of order of magnitude is strictly correct for reflections from a crystal of constant thickness. Comparison of equations 1 and 2 shows that the factor required to convert intrinsic breadth to breadth on the film is

$$\frac{\beta_f}{\beta_i} = \frac{\lambda}{T\cos\theta}\,\frac{T}{d} = 2\tan\theta \tag{3}$$

The assumption of a constant thickness T for the crystal is, however, unnecessary, the argument leading to Bragg's law depends only on the coherence of rays scattered in the immediate neighbourhood of the line BY bisecting the angle between the incident and reflected x-rays For a crystal of varying thickness the intensity of reflection, total or peak, will be obtained by adding the intensities, total or peak, produced by rays scattered in the neighbourhoods of all the lines of variable length parallel to BY, *Figure 6* The unit scatterer has so far been taken as a lattice plane, it will now be necessary to take a unit with volume and content equal to those of the unit cell If the volume of the unit cell is U, and the spacing of the lattice planes parallel to BY is d, then the number of lines/cm² of such units parallel to BY will be d/U Choose an x axis parallel to BY, and y and z axes perpendicular to it Then the peak intensity will be given by the sum, for all lines of units parallel to BY, of $(T/d)^2$, where T is the length of the lines Since the units are small compared with the total volume V of a crystal, the sum may be written as the integral over the cross section of the crystal of $(T/d)^2$ multiplied by the number of lines/cm², or

$$\begin{aligned} P_i &= \iint (T/d)^2(d/U)\,\mathrm{d}y\,\mathrm{d}z \\ &= (Ud)^{-1}\iint T^2\,\mathrm{d}y\,\mathrm{d}z \end{aligned} \tag{4}$$

Since $T = \int \mathrm{d}x$ this may be written more compactly

$$\begin{aligned} P_i &= (Ud)^{-1}\iiint T\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \\ &= (Ud)^{-1}\int_V T\,\mathrm{d}V \end{aligned} \tag{5}$$

where the integration extends throughout the volume V of the crystal The total intensity of the reflection is the total number of unit cells, $I_i = V/U$, so that the intrinsic breadth is

$$\beta_i = I_i/P_i = Vd\Big/\int_V T\,\mathrm{d}V \tag{6}$$

giving

$$\beta_f = \lambda V/\cos\theta\int T\,\mathrm{d}V \tag{7}$$

for the breadth on the film

Equation 7 shows that the thickness of a uniformly thick crystal is given by $\lambda/\beta_f\cos\theta$ For crystals of varying thickness it is often convenient to define an apparent particle size ε by

$$\varepsilon = \lambda/\beta_f\cos\theta = V^{-1}\int_V T\,\mathrm{d}V \tag{8}$$

The integral in this equation has been evaluated for the *hkl* reflections from several regular crystal shapes[8-12]

BROADENING BY MISTAKES

In the preceding paragraphs the intensity scattered by a single cell has been taken as the unit of scattering When the unit cells differ in their scattering power, as they must if mistakes in their arrangement are to produce any observable effect, the actual scattering power of the cell must appear explicitly in the intensity expressions The unit of scattering is taken as that of a single free electron, and that of a cell is given by F, where $F^2 = A^2 + B^2$, A being the amplitude of the part of the scattering by the cell in phase, and B the part in quadrature, with that which would be scattered by an electron at the origin Consider a line n units long perpendicular to the reflecting planes, *Figure 6* Because of the mistakes the scattering factors of these will not all be the same If the scattering of the first unit is given by A_1, B_1, that of the second by A_2, B_2, and so on, the intensity scattered by the whole line will be given by

$$G^2 = X^2 + Y^2 \tag{9}$$

$$\text{where}\qquad \begin{aligned} X &= A_1 + A_2 + A_3 + \cdots \\ Y &= B_1 + B_2 + B_3 + \cdots \end{aligned}$$

These equations give for the intensity of scattering

$$\begin{aligned} G^2 = {} & (A_1^2 + B_1^2) + (A_2^2 + B_2^2) + \cdots \\ & + 2\{(A_1A_2 + B_1B_2) + (A_2A_3 + B_2B_3) + \cdots\} \\ & + 2\{(A_1A_3 + B_1B_3) + (A_2A_4 + B_2B_4) + \cdots\} \\ & + \cdots \\ & + 2(A_1A_n + B_1B_n) \end{aligned} \tag{10}$$

where the terms have been arranged so that in the first line the factors multiplied refer to the same unit, in the second line to consecutive units, in the third line to units separated by one intervening unit, and so on.

The number of terms of the type $(A_j^2 + B_j^2)$ is n, of the type $(A_jA_{j+1} + B_jB_{j+1})$ is $n-1$, of the type $(A_jA_{j+m} + B_jB_{j+m})$ is $n-m$. If we represent by J_m the average value of $(A_jA_{j+m} + B_jB_{j+m})$, the sum may be written

$$G^2 = nJ_0 + 2(n-1)J_1 + 2(n-2)J_2 + \dots + 2(n-m)J_m + \dots + 2J_{n-1} \qquad (11)$$

The calculation of J_m, once the type of mistake occurring in the crystal has been guessed, is an exercise in probability theory[8, 14–19]. Ordinarily it is found that J_m decreases practically to zero for a value of m large compared with unity but small compared with n. The sum in equation 11 may then be replaced by an integration, so that

$$G^2 = 2\int_0^n (n-m)J_m \mathrm{d}m$$

$$= 2n\int_0^\infty J_m \mathrm{d}m \qquad (12)$$

to an approximation valid in the circumstances mentioned. Summing for all parallel lines of units, to give the intensity diffracted by the whole crystal, merely introduces N, the total number of units in the crystal, instead of n, the number of units in one line. Equation 12 then becomes

$$P_s = 2Nd^{-1}\int_0^\infty J_t dt \qquad (13)$$

where $t = md$ is a distance measured perpendicular to the reflecting planes. The breadth on the film then becomes

$$\beta_f = \lambda J_0/2\cos\theta \int_0^\infty J_t \mathrm{d}t \qquad (14)$$

since the total intrinsic intensity is NJ_0.

In this discussion of mistake broadening it has been tacitly assumed that the average value of $(A_jB_{j+m} - A_{j+m}B_j)$ is zero. If this is not so the peak of the line is displaced as well as broadened. Such displacements are common among the clay minerals, and have been described by D. M. C. MACEWAN[20]. The problem is rather complicated, and only references can be given here[8, 14, 21]. Complete layer disorder, also found in some clay minerals, leads to peculiar 'tailed' reflections; these[23, 24] and diffraction by random linear structures[25] are also difficult to discuss by elementary methods.

Space does not permit a discussion of particular substances, but the assumption of random mistakes gives a reasonably good explanation of the line broadening in hexagonal cobalt[15, 26] and suitably annealed $AuCu_3$[25, 18, 27–30]. With the latter it is interesting to find that the mistakes mostly occur in a way that does not bring the gold atoms into contact with one another, even along the fault planes. Powder photographs are not, however, ideally suited for the complete verification of the postulated types of mistake, and whenever single crystals are obtainable an investigation of the distribution of intensity in reciprocal space is desirable. The single-crystal photograph of zinc sulphide *Figure 7* for example shows not only which reflections are broadened and by how much, information obtainable from a powder photograph, but also shows directly *1* that the mistakes are layer displacements, and *2* which layers are displaced. This additional information might be inferred from a powder photograph and a knowledge of the crystal structure, but could not be directly verified.

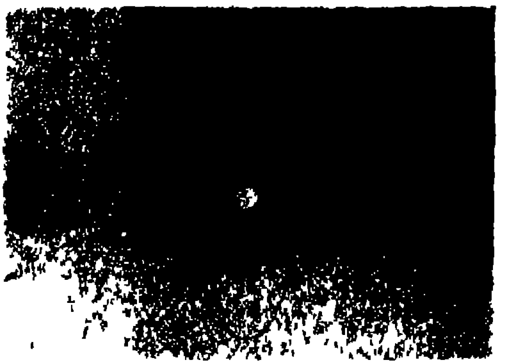

Figure 7 Rotation photograph of zinc sulphide, 6-layer structure disordered towards 2-layer structure. The streaks connect spots with same values of hk, different l, indicating layer displacements perpendicular to c axis

STRAIN BROADENING

In distorted crystals the size of the unit cell varies; the derivation of Bragg's law shows that only the variation of the interplanar spacing of the reflecting planes is significant in producing incoherence of the scattered rays. It must be emphasized that it is variation that produces the broadening; a uniformly expanded or contracted lattice (constant strain) would give displaced lines, not broadened lines. Sinusoidally distorted crystals give interesting satellite lines[31–37] comparable to the 'side bands' resulting from modulation in electronic circuitry, but the study of various aperiodic distortions[38–48], in the hope of throwing light on the state of cold worked metals, may be of more practical importance. Perhaps the simplest of these is a bent crystal lamella, *Figure 8*. Such bent lamellae would arise, for example, in the process of 'kinking' described by E. OROWAN[49]. The longitudinal strain at a distance x from the central axis is x/R, resulting in a normal strain of $-\sigma x/R$, where R is the radius of curvature and σ is the appropriate Poisson's ratio. The interplanar spacings of planes parallel to the lamella are thus

$$d = d_0(1 - \sigma x/R) \qquad (15)$$

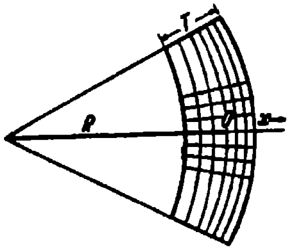

Figure 8 Bent crystal lamella, showing variation of interplanar spacing (exaggerated)

and the displacements $u(x)$ of the planes from their positions in the unbent lamella are

$$u(x) = \sigma x^2/2R \tag{16}$$

The thickness T_c of the coherently reflecting region is given in order of magnitude by

$$(\sigma T_c^2)/(2R) \sim d/2$$

$$T_c \sim [(Rd)/\sigma]^{\frac{1}{2}} \tag{17}$$

The intrinsic peak intensity is therefore given by

$$P_i \sim (T_c/d)^2 = R/\sigma d \tag{18}$$

The total intensity, however, remains T/d, so that the intrinsic integral breadth is

$$\beta_i \sim \frac{T}{d}\ \frac{\sigma d}{R} = \frac{\sigma T}{R} \tag{19}$$

Multiplication by $2\tan\theta$ gives for the breadth on the film

$$\beta_f \sim (2\sigma T/R)\tan\theta \tag{20}$$

The broadening is therefore proportional to $\tan\theta$, and independent of λ, in contrast with particle-size broadening, which is proportional to $\lambda\sec\theta$ As it stands, equation 20 applies only to reflections from planes parallel to the faces of the lamella For other planes it has been found[41] that

$$\beta_f = (2T/R)\left|q^2 - \sigma p^2\right|\tan\theta \tag{21}$$

where p is the cosine of the angle between the plane normal and the x axis and q is the cosine of the angle between the plane normal and a y axis chosen perpendicular to x in the plane of bending

In deriving equations 16 to 20 it has been tacitly assumed that T_c is considerably smaller than T i e that coherence is limited by the distortion, not by the thickness of the lamella The condition for this to occur is that

$$(2Rd/\sigma)^{\frac{1}{2}} \ll T$$

which reduces to

$$(\sigma T^2\sin\theta)/R\lambda \gg 1 \tag{22}$$

The more exact analysis gives instead

$$\frac{\left|q^2 - \sigma p^2\right| T^2\sin\theta}{pR\lambda} \gg 1 \tag{23}$$

which differs only in introducing the direction cosines p and q We see, therefore, that a sufficiently thin lamella will not give distortion broadening, since this condition will not be fulfilled, in fact if the above ratio is much less than unity it will give particle-size broadening with

$$\beta_f = p\lambda/T\cos\theta \tag{24}$$

For intermediate values of the ratio there is a complicated transition from one form of broadening to the other[41]

Equations 20 and 21 have the form

$$\beta_f \sim e_m\tan\theta \tag{25}$$

where e_m is the maximum strain in the direction perpendicular to the reflecting planes, and there is a numerical factor of the order of 4 The maximum strain in a heavily cold worked material may be expected to be of the order of magnitude of the macroscopic yield stress divided by the appropriate value of Young's modulus F_Y In cubic crystals the latter is given by

$$(E_Y)_{hkl} = s_{11} - 2(s_{11} - s_{12} - 2s_{44})H \tag{26}$$

where

$$H = (k^2l^2 + l^2h^2 + h^2k^2)/(h^2 + k^2 + l^2)^2 \tag{27}$$

h,k,l are the indices of the reflection and s_{11}, s_{12}, s_{44} are elastic constants If the yield stress Y does not vary greatly with direction, the broadening should be given by

$$\beta_f \sim 4\,Y\{s_{11} - 2(s_{11} - s_{12} - 2s_{44})H\}\tan\theta \tag{28}$$

A R STOKES, K J PASCOE and H LIPSON[44], and H D MEGAW, H LIPSON and A R STOKES[45, 46] have found that this equation is in quite good agreement with experiment, but C S SMITH and E F STICKLEY[47] found only qualitative agreement A. R STOKES and A J C. WILSON[48] and N M BLACHMAN[49] have discussed the relations between broadening and indices of reflection to be expected on other assumptions regarding the relationship between stress and strain All are of the same general type as equation 28, but the way in which H and the elastic constants enter is different The experimental results so far have not been sufficiently accurate to decide which is the closest approximation to the actual state of a cold worked metal

It would not be fair, however, to end this section without remarking that W A WOOD and W A. RACHINGER[49-51] do not accept the view that line broadening by cold worked metals is due primarily to lattice distortions They prefer to interpret the broadening in terms of a crystallite size, and it happens that their crystallite sizes are the right order of magnitude to fit in with Bragg's theory of the strength of metals[51, 52] H Lipson and A R Stokes[55] have disputed Wood's evidence, and the question remains in a rather unsatisfactory state

The author thanks Dr R L Griffith, Research Laboratories, Eastman Kodak Company, Rochester, N Y, for permission to reproduce Figure 7

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Absorption of Sound by Porous Materials

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SOUND absorbing materials are employed for the control of reverberation in auditoria, in order to provide appropriate conditions for satisfactory hearing of speech and music, and for the reduction of noise The design of such materials has often proceeded largely along empirical lines based upon direct measurements of sound absorption Theoretical consideration of the mechanisms by which sound is absorbed provides a better insight into the manner in which various physical characteristics of a material may influence its sound absorbing properties, and leads to a more scientific basis of design

Absorption of sound by the walls of rooms may be brought about in three essentially different ways First, glass panels and wood partitions may absorb the sound because they are set in motion by impinging sound waves, the motion being damped principally along the edges of the panels, thus transferring sound energy into heat A second mechanism is that provided by resonant cavities, the necks of which offer resistance to the vibrating air, by which again sound energy is dissipated[1] The third mechanism is the one shown by porous materials and this article is devoted to it Almost all materials that have been marketed as special sound absorbing materials belong to this class Combinations of porous materials with perforated front walls of non-porous material are not uncommon In these pure porosity effects are combined with resonance effects Lack of space prevents us however from including these in this review

We shall further restrict ourselves to the case of sound waves impinging normally on a wall of infinite dimensions It is frequently possible to deduce the absorption at oblique incidence[2] by substituting $z \cos\varphi$ for z in the formulae, where z is the specific acoustic impedance (to be defined later) of the wall material and φ the angle between the normal and the direction of propagation of the incident sound, z characterizes the material as regards its acoustical behaviour including sound absorption As $z \cos\varphi$ is generally smaller than z the wall is 'softer' for oblique incidence and as a rule absorbs more The absorption coefficient for random incidence therefore is greater than the absorption coefficient for normal incidence A value of 1 4 for this ratio is a representative one

As regards the second restriction, it may be mentioned that the absorption per unit of area is not constant, small samples as a rule absorbing relatively more than large samples This is due to diffraction effects along the edges of the sample Although the absorptive power of wall treatments is usually calculated from the areas A_i of the different parts of the wall and their absorption coefficients a_i by adding the products $A_i a_i$, more accurate measurements have proved that this is only a first approximation. A comparison, *Figure 1*, of measurements of absorption coefficients by reverberation methods performed in different laboratories reveals discrepancies that have to be explained by the differences in shape of test rooms, arrangement of material and size of samples[3]

INTERFEROMETER ACOUSTIC IMPEDANCE

The influence of size of the test sample can be avoided by measuring the materials by interferometer methods[4] In these methods sound waves move to and fro in a cylindrical tube terminated at one end by the test sample, and in one method the sound pressure is measured along the standing wave system, the ratio of the maximum and minimum values together with the location of these extremes being the data from which the acoustical impedance of the sample can be calculated, *Figure 2*

The pressure at the position x at time t can be expressed by (the real part of)

$$p(x,t) = p_i \exp j\omega(t - x/c_0) + p_r \exp j\omega(t + x/c_0 + \Delta/\omega)$$

The first term represents the incident wave of amplitude p_i, angular frequency ω and propagation velocity c_0 The index $_0$ refers to free air The second term represents the reflected wave Its amplitude is p_r At $x = 0$, which is taken to be the location of the sample, a phase shift of Δ radians is shown From the measurement of p for all values of x the constants p_i, p_r and Δ may be determined

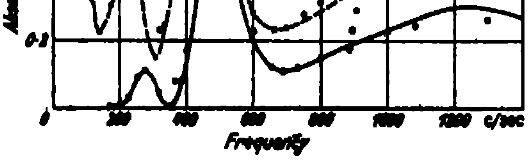

Figure 1 Comparison of reverberation measurements ●— — —● with interferometer measurements ○—○ performed on the same sample

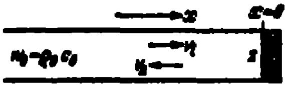

Figure 2 Interferometer

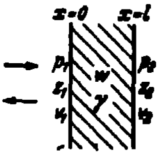

Figure 3 Relation between input and output impedance

For the particle velocities in the standing wave system a similar formula applies and it is necessary here to subtract as the velocities add vectorially

$$v(x,t) = v_i \exp j\omega(t - x/c_0) - v_r \exp j\omega(t + x/c_0 + \Delta/\omega)$$

In both incident and reflected waves, taken separately, pressure and particle velocity are in phase with each other, this applies for all plane waves in free air (compare p 402) and their quotient is constant in time and called the wave impedance w_0

$$w_0 = p_i/v_i = p_r/v_r \qquad (1)$$

At the surface of the sample, $x = 0$ and we have, in particular

$$p(0) = (p_i + p_r \exp j\Delta) \exp j\omega t \qquad (2)$$

$$v(0) = (v_i - v_r \exp j\Delta) \exp j\omega t \qquad (3)$$

and from equations 1, 2 and 3 the quotient of p and v at this position is found to be

$$z = w_0 \frac{p_i + p_r \exp j\Delta}{p_i - p_r \exp j\Delta} \qquad (4)$$

which will be called the acoustic impedance of the wall This quantity will in general be complex and this is another way of saying that the two quantities represented by numerator and denominator are not in phase As p_i, p_r and Δ are measured in the interferometer and w_0 is known, z may be considered as also being known Inverting the last formula

$$r = \frac{p_r \exp j\Delta}{p_i} = \frac{z - w_0}{z + w_0} \qquad (5)$$

which quotient is called the complex reflection coefficient The square of its absolute value is the ratio of reflected to incident energy and the absorption coefficient is the complement of this ratio

$$\alpha = 1 - \left(\frac{p_r}{p_i}\right)^2 = 1 - \left|\frac{z - w_0}{z + w_0}\right|^2 \qquad (6)$$

Knowledge of z thus automatically involves knowledge of the sound absorption coefficient

WAVE IMPEDANCE AND PROPAGATION CONSTANT

The acoustic impedance of a layer of a certain thickness will be a function of this thickness l and furthermore will depend on what lies at the back of the layer The nature of the backing will be irrelevant for a layer of infinite thickness, when the impedance is called the wave impedance w In contrast to z which is dependent on the thickness, w is a specific quantity determined purely by the nature of the material A second specific quantity is the propagation constant γ As a wave moves forward through the medium it will be damped exponentially, so that the pressure is represented by

$$p = \text{constant} \times \exp j\omega(t - x/c) \times \exp(-\alpha x) \qquad (7)$$

where α is called the attenuation constant Rearranging the factors it is seen that p — and in an infinite medium v also — contains the factor

$$\exp[-\{\alpha + j(\omega/c)\}x]$$

Denoting ω/c by β, the so-called phase constant, we take $\alpha + j\beta$ together as γ, so that p and v are both proportional to $\exp(-\gamma x)$

We shall now proceed to calculate the impedance of a layer of thickness l, backed by an arbitrary impedance z_2 at the far end, *Figure 3* The pressure in the standing wave system within the layer will be

$$p = [p_i \exp\{-\gamma(x - l)\} + p_r \exp\{-\gamma(l - x)\} \exp j\Delta] \exp j\omega t \qquad (8)$$

and the 'velocity' will be

$$v = [v_i \exp\{-\gamma(x - l)\} - v_r \exp\{-\gamma(l - x)\} \exp j\Delta] \exp j\omega(t - \chi/\omega) \qquad (9)$$

Velocity is quoted above because by this word is meant the volume of air moving in unit time through unit area and, in a porous medium where part of the volume is occupied by the solid material, this is not the same as the actual velocity of the air Furthermore, a phase difference χ was introduced between pressure and velocity of each partial wave In other words the wave impedance

$$w = \frac{p_i}{v_i} = \frac{p_i \exp j\chi}{v_i} = \frac{p_r}{v_r} = \frac{p_r \exp j\chi}{v_r}$$

is supposed to be complex Following the manner of deducing equation 5, it is now found that

$$\frac{p_r \exp j\Delta}{p_i} = \frac{z_2 - w}{z_2 + w}$$

Introducing the last two equations into the formulae for p and v and looking in particular for the values at $x = 0$, then

$$p_1 = p_i \left[\exp \gamma l + \frac{z_2 - w}{z_2 + w} \exp(-\gamma l)\right] \exp j\omega t$$

$$v_1 = v_i \left[\exp \gamma l - \frac{z_2 - w}{z_2 + w} \exp(-\gamma l)\right] \exp j\omega\left(t - \frac{\chi}{\omega}\right)$$

from which

$$z_1 = \frac{p_1}{v_1} = w\frac{z_2 \cosh \gamma l + w \sinh \gamma l}{z_2 \sinh \gamma l + w \cosh \gamma l}$$

and this is the general relation between z_1 and z_2

Interesting cases are those where $z_2 = \infty$ (hard back wall) and where $z_2 = 0$ (for the realization of which see below) It is found that

$$\left.\begin{array}{lll} \text{for } z_2 = \infty & z_1(\infty) = w \operatorname{cotanh} \gamma l \\ \text{for } z_2 = 0 & z_1(0) = w \tanh \gamma l \end{array}\right\} \quad (10)$$

so that from measurements of $z_1(\infty)$ and $z_1(0)$ (in electrical language, the input impedances for open and short-circuited transformer secondary respectively) w and γ can now be calculated separately

$$w^2 = z_1(\infty)\ z_1(0)\,, \quad \tanh^2 \gamma l = z_1(0)/z_1(\infty) \qquad (11)$$

If the layer consists of air, for which the wave impedance w_0 is real and γ is purely imaginary, it is found that

$$z_1(\infty) = -j\, w_0 \cot \omega l/c_0 \qquad (12)$$

and this provides an impedance of zero for certain values of the thickness l of the layer, namely if $l = (2n + 1)$ quarter wavelengths The artifice of backing a layer of an arbitrary material by zero impedance is therefore to provide a clearance of a certain thickness between the back of the sample and a hard wall

DENSITY AND BULK MODULUS

It has been shown in the foregoing sections how the specific quantities wave impedance and propagation constant can be determined experimentally and how they are connected with sound absorption Alternatively, these quantities can be deduced from other specific quantities that are not primarily of an acoustical nature As an introduction consider free air The equation of motion for the particles in a longitudinal wave is

$$-\frac{\partial p}{\partial x} = \varrho_0 \frac{\partial v}{\partial t} \qquad (13)$$

where ϱ_0 is the density (specific mass) The equation of continuity is

$$-\frac{\partial v}{\partial x} = \frac{1}{K_0}\frac{\partial p}{\partial t} \qquad (14)$$

where K_0 is the compression (or bulk) modulus. For a sinusoidal wave

$$\partial/\partial x = -\gamma \qquad \partial/\partial t = j\omega$$

so that the equations can also be written in the forms:

$$\gamma p = j\omega\varrho_0 v \qquad (13a)$$

$$\gamma v = j\omega p/K_0 \qquad (14a)$$

from which

$$\gamma^2 = -\omega^2 \varrho_0/K_0 \text{ and therefore } c_0^2 = K_0/\varrho_0 \qquad \dots.(15)$$

and

$$w^2 = \varrho_0 K_0 \qquad (16)$$

and it is seen that γ is purely imaginary ($\alpha = 0$) and that w is real

Now for air enclosed in a porous material, alterations must be applied to the equations of both motion and continuity, due to internal structure, viscosity and heat conduction The two last mentioned effects are responsible for the transformation of sound energy into heat and consequently for the sound absorption

In what follows generalized equations of motion will be deduced in which in addition to the inertia term in $\partial v/\partial t$ on the right hand side of equation 13 there will be a friction term in v Now as $v = (1/j\omega)\,(\partial v/\partial t)$ the right hand side can be written as $\partial v/\partial t$ multiplied by a complex number which will be called the complex density ϱ In a similar way the equation of continuity has to be modified in general as the rate at which the volume changes $\partial v/\partial x$ depends not only on changes of pressure, as expressed in equation 14, but also on temperature changes This leads to a generalized complex bulk modulus K, taking the place of K_0 of equation 14 In the generalized case wave impedance and propagation constant will be deduced in a way similar to that followed to obtain equations 15 and 16

$$\gamma^2 = -\omega^2 \varrho/K \qquad (17)$$

$$w^2 = \varrho K \qquad (18)$$

Both w and γ will in general be complex

The complexity of ϱ is attributed to viscosity effects, that of K to temperature effects Some doubt as to the correctness of these assumptions may be felt and justification is required This is possible[8] but having regard to the space available they will be taken for granted

CIRCULAR PORES

If air vibrates parallel to a plane wall, the air in contact with the wall will remain at rest and on account of viscosity a layer of a certain thickness will be influenced by the proximity of the wall and will vibrate with a smaller amplitude than layers at greater distances Assuming approximately a linear variation of the velocity with distance from the wall, the viscosity force on a layer of thickness δ will be $\eta v/\delta$ per unit area of wall, where η stands for the viscosity (171×10^{-6} c g s units for air). Compare this with the inertia force experienced by the same layer

$$\varrho_0\, \delta\, \partial v/\partial t = j\omega\varrho_0 \delta v$$

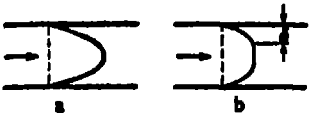

Figure 4 Comparison of a *Poiseuille flow with* b *Helmholtz flow*

Both forces will be of the same order of magnitude if

$$\delta^2 \approx \eta/\omega\varrho_0 \qquad (19)$$

and thus δ is a good value for the depth of the layer that we may look upon as hindered in its motion by the wall

Now let air vibrate longitudinally in a cylindrical conduit Whether the gas in the centre of the conduit will experience some influence from the wall will depend on whether the radius R of the conduit is smaller than δ or not As a useful dimensionless parameter we therefore introduce the ratio of R to δ

$$\mu = R/\delta = (\omega R^2\varrho_0/\eta)^{\frac{1}{2}} \qquad (20)$$

which for a certain type of conduit will run from low to high values if the frequency does the same, note that it varies as the square root of the frequency

For sufficiently low frequencies (or for sufficiently narrow pores) $\delta \gg R$ and we have to deal with Poiseuille's law, completed with an inertia term

$$-\frac{\partial p}{\partial x} = \frac{8\eta}{R^2}v + \frac{4}{3}\varrho_0\frac{\partial v}{\partial t} \qquad (21)$$

It may strike the reader that the factor 4/3 has also been added This is a consequence of the fact that the velocity distribution over the cross section of the conduit is parabolic In this equation v represents the average velocity The complex density is

$$\varrho = \frac{4}{3}\varrho_0 - j\frac{8\eta}{\omega R^2} = \frac{4}{3}\varrho_0\left(1 - j\frac{6}{\mu^2}\right) \qquad (22)$$

If on the other hand $\delta \ll R$ (high frequencies or wide channels) there is only a relatively thin viscosity layer and Poiseuille's law no longer applies Instead, a flow law due to Helmholtz is valid, *Figure 4*

$$-\frac{\partial p}{\partial x} = \varrho_0\frac{\partial v}{\partial t} + \frac{2}{R}(j\eta\varrho_0\omega)^{\frac{1}{2}}v \qquad (23)$$

with a complex density

$$\varrho = \varrho_0[1 + 2(-j^{\frac{1}{2}}/\mu)] \qquad (24)$$

The general problem of finding the value of ϱ for all intermediate values of μ has been solved by J B CRANDALL[6] and the result is

$$\varrho = \varrho_0\bigg/\left(1 - \frac{2}{\mu(-j)^{\frac{1}{2}}}\frac{J_1[\mu(-j)^{\frac{1}{2}}]}{J_0[\mu(-j)^{\frac{1}{2}}]}\right) \qquad (25)$$

where J_0 and J_1 are Bessel functions The contour of ϱ in the complex plane is shown in *Figure 5*

For the bulk modulus it is relatively simple to indicate its values in the two limiting cases of very low and very high frequencies At low frequencies there is sufficient time for heat exchange between gas and wall and the process will be isothermal The bulk modulus can then be calculated from Boyle's law

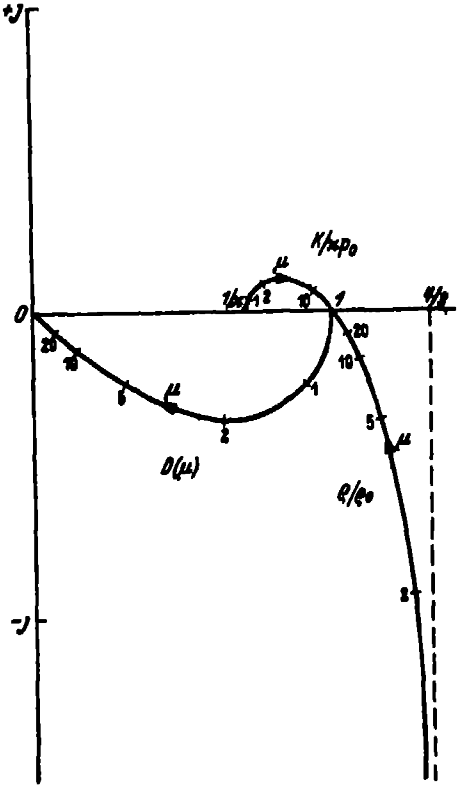

Figure 5 Representation of the contours of ϱ/ϱ_0, $K/\varkappa p_0$ *and* $D(\mu)$ *in the complex plane*

$$\frac{dp}{p_0} = \frac{d\varrho}{\varrho_0}$$

giving

$$K = \varrho_0\frac{dp}{d\varrho} = p_0$$

At high frequencies the temperature changes of the gas will follow each other so rapidly that there is hardly any heat exchange with the wall, the process is adiabatic and Poisson's law holds

$$\frac{dp}{p_0} = \varkappa\frac{d\varrho}{\varrho_0}$$

where $\varkappa$ is the ratio of the two specific heats c_p/c_v, $\varkappa$ has the value 1 4 for diatomic gases like air Obviously

$$K = \varkappa p_0$$

In both these limiting cases pressure and density are in phase In intermediate conditions however the gas will, for the same value of pressure, be hotter during compression than during expansion and the density will be smaller during the former The p/ϱ diagram is elliptic in shape, p and ϱ are out of phase and the bulk modulus is complex It is shown as a function of μ in *Figure 5* and the general formula is[7]

$$K = \kappa p_0 \Big/ \left(1 + \frac{2(\kappa - 1)}{B\mu(-j)^{\frac{1}{2}}} \frac{J_1[B\mu(-j)^{\frac{1}{2}}]}{J_0[B\mu(-j)^{\frac{1}{2}}]}\right) \tag{26}$$

where $B = (\eta\kappa c_p/\lambda)^{\frac{1}{2}}$ and λ = heat conductivity B is dimensionless and for air and other diatomic gases is equal to 0 86 If it were exactly unity, the same function of μ would have been found in the formulae for both ϱ and K, namely

$$D(\mu) = \frac{2}{\mu(-j)^{\frac{1}{2}}} \frac{J_1[\mu(-j)^{\frac{1}{2}}]}{J_0[\mu(-j)^{\frac{1}{2}}]} \tag{28}$$

Putting $B = 1$ deliberately only means a little shift along the K contour Besides, as soon as real materials are considered, it will be found that the internal structure has such influence that a shift in the same sense has to be made Therefore, disregarding factor B, we may write

$$\varrho = \frac{\varrho_0}{1 - D(\mu)}, \quad K = \frac{\kappa p_0}{1 + (\kappa - 1)\, D(\mu)} \tag{28}$$

$D(\mu)$ is complex and may be represented graphically in the complex plane, see *Figure 5*

It is not surprising that the same function of μ influences both viscosity and heat exchange Each phenomenon is caused by thermal diffusion of gas molecules and one cannot manifest itself without the other

For the regions of either high or low values of μ relatively simple formulae may be derived for $D(\mu)$ by expansion of the Bessel functions Thus

for low values of μ

$$D = 1 - (j/8)\,\mu^2,\ D(0) = 1 \tag{29}$$

for high values of μ

$$D = [2(-j)^{\frac{1}{2}}]/\mu,\ D(\infty) = 0 \tag{30}$$

With the help of these approximations for D the corresponding approximations for ϱ and K may be calculated For ϱ formulae 22 and 24 result, while for K we are led to the following

for low values of μ

$$K = p_0[1 + j\mu^2(\kappa - 1)/8\kappa] \tag{31}$$

for high values of μ

$$K = \kappa p_0\,[1 - 2(-j)^{\frac{1}{2}}(\kappa - 1)/\mu] \tag{32}$$

INTERNAL STRUCTURE

Formula 28 would apply directly to a wall with a 'honeycomb structure' (a term introduced by Lord RAYLEIGH) if the partition walls between the cells can be considered very thin If the axes of the cells are placed obliquely with respect to the front surface so that they make an angle φ with the normal, there will be room for only *cos φ times the number of* cells that would be present with perpendicular axes Moreover, along the direction of the axis the pressure gradient will be smaller, the factor again being cos φ The amount of air streaming in and out will be decreased and the apparent density therefore increased, the latter by the factor $1/\cos^2\varphi$ This factor will be called the structure factor and in general will be denoted by k' Where pores are running in all directions we shall have to determine an average value for $1/\cos^2\varphi$ and for random distribution of φ this average amounts to $k' = 3$

There may be other reasons why the density seems to be increased If parts of the open space have the character of side cavities debouching into main conduits, that portion of air enclosed in these cavities will hardly take part in the air flow, the average velocity will therefore be too small and k' will contain a factor equal to the ratio of the total air content to that of the main pores Finally parts of the solid material might vibrate together with the air, again giving rise to a contribution to k' It appears that for practical materials k' may take all values from 1 up to 15

The compressibility is far less influenced by this internal structure than the density If the side cavities debouch into the main pores through narrow conduits of high resistance, it may be expected that at higher frequencies these side cavities would become inactive as a buffer volume, so that K would increase with frequency During transition from activity to inactivity the side pores might even make a complex contribution to K If, however, this particular case does not occur, the internal structure has no influence on the compressibility and this will be taken as the common condition

A porosity deviating from unity will influence both the apparent density and the compressibility Since v denotes the volume displaced in unit time through unit area, it will be directly proportional to the porosity h, which in the equation of motion is accounted for by multiplying ϱ by $1/h$ and in the equation of continuity by multiplying K by the same factor In order to be applicable to real porous materials, formulae 28 for ϱ and K have then to be modified to

$$\varrho = \frac{k'}{h} \frac{\varrho_0}{1 - D(\mu)} \qquad K = \frac{1}{h} \frac{\kappa p_0}{1 + (\kappa - 1)\, D(\mu)} \tag{33}$$

Introducing these values into equations 17 and 18 it is found that the propagation constant is proportional to $\sqrt{k'}$ and that the wave resistance is proportional to $\sqrt{k'}/h$

The effective pore radius R', which must be known in order to calculate μ for all frequencies, is determined from the resistance offered by a layer of unit thickness to a continuous stream of air. This resistance per unit surface area follows from equation 21 by disregarding the inertia term and by introducing the factor k'/h

$$\text{specific flow resistance } \sigma = (k'/h)\,(8\eta/R'^2) \tag{34}$$

In structures with side cavities the condition may occur that the radius of the cavity, considered as a sphere, is much greater than the radius of the pores carrying the stream. It is then possible that the low frequency (isothermal) value of ϱ has to be combined with the high frequency (adiabatic) value of K. As μ is determined from flow resistance at low frequency it would mean that the value of μ to be used for the calculation of K has to be increased and that it may be necessary to make a shift along the K contour in the complex plane. In all practical materials a shift of this nature will be necessary, although generally a small one. This was anticipated when the value unity was substituted for the constant B. In view of the complexity of the theory and the small influence of an eventual shift on the results there is little sense in looking for a better approximation than the one obtained by simply putting $B = 1$

ABSORPTION COEFFICIENT

With the above considerations the acoustic behaviour of most porous materials can be explained adequately, the material being characterized by its porosity, specific flow resistance, structure factor and thickness. Unfortunately there is no method of measuring structure factors other than acoustically so that a prediction of the acoustical behaviour entirely from non-acoustical measurement data is not possible

Figure 6 shows absorption coefficients determined by the interferometer method of a number of materials for which agreement between theory and experiment is established. The specific data are

Material	*Thickness* l *mm*	*Porosity* h	*Structure factor* k'	*Specific flow resistance c.g.s. units*
J M Permacoustic	25	1·0	13	160
Hair felt	20	0 95	3	70
Acoustic plaster	21	0 70	3 3	10

For the regions of low and high frequencies relatively simple formulae may be derived starting from the approximations for D, equations 29 and 30 above, first leading to the approximations for ϱ equations 22 and 24 and then for K equations 31 and 32. From these the wave impedance and propagation constant are evaluated, at the same time introducing h and k'

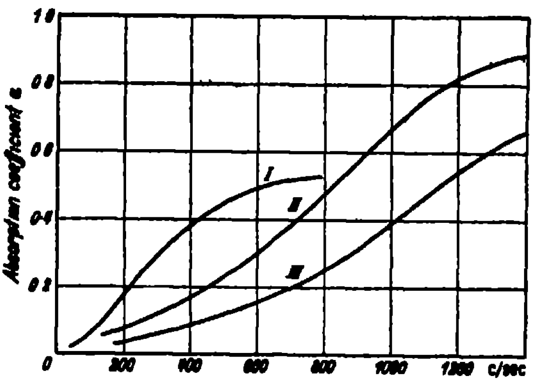

Figure 6 Absorption characteristics of I J M Permacoustic, II hair felt, III acoustic plaster

for low frequencies

$$\mu \ll 1 \qquad \gamma^2 = j\frac{\omega^2}{\mu^2}\frac{8k'\varrho_0}{p_0}$$

$$w^2 = -j\frac{1}{\mu^2}\frac{8k'}{h^2}\varrho_0 p_0$$

for high frequencies

$$\mu \gg 1 \qquad \gamma^2 = -k'\frac{\omega^2}{c_0^2}$$

$$w^2 = \frac{k'}{h^2}\varrho_0^2 c_0^2$$

For the function cotanh γl, occurring in formula 10 for z, there are the following expansions

for low frequencies

$$\text{cotanh}\,\gamma l = \frac{1}{\gamma l} + \frac{\gamma l}{3}$$

for high frequencies

$$\text{cotanh}\,\gamma l = 1$$

As a consequence of all this the impedance at low frequencies of a layer of thickness l will be

$$z = -j\frac{p_0}{h\omega l} + \frac{8}{3}\frac{k'}{h}\frac{\omega}{\mu^2}\varrho_0 l \tag{35}$$

The first term is large and imaginary, the second term is real and independent of frequency, as μ^2 is proportional to ω

Calculating the absorption coefficient with the help of

$$1 - \alpha = \left|\frac{z - \varrho_0 c_0}{z + \varrho_0 c_0}\right|^2$$

reveals for low frequencies

$$a = \frac{32}{3}\,k'h\kappa^2\,\frac{\omega^2}{\mu^2}\,\frac{l^2}{c_0^2} = \frac{4}{3}\,\frac{\kappa^2}{\varrho_0 c_0^2}\,h^2\,\sigma\,l^2\,\omega^2 \qquad (36)$$

It is seen that at low frequencies a starts as a parabolic function of frequency

In the limit at high frequencies it is seen that the propagation constant tends to become purely imaginary and, as l becomes large with respect to wavelength, this case can be treated as that of the reflection of waves coming from a medium with wave impedance $\varrho_0 c_0$ (the free air) on to a medium with wave impedance $(\sqrt{k'/h})\varrho_0 c_0$ The absorption coefficient here is calculated from

$$1 - a = [(\sqrt{k'} - h)/(\sqrt{k'} + h)]^2 \qquad (37)$$

and with the help of this formula it is possible to determine k' for a material of known h from the measurement of the absorption coefficient at high frequencies

ELASTIC FRAME

A number of materials cannot be covered by the foregoing treatment and this is due to vibrations in the solid frame itself Although the frames of all materials are to a certain degree elastic this point can be disregarded for acoustic plasters, wood fibre boards and even for felts This is not so however for rubber-like skeletons

In these examples both solid material (index 1) and enclosed air (index 2) vibrate with a certain mutual coupling The equations of motion are, again using generalized densities

$$\begin{aligned} -\frac{\partial p_1}{\partial x} &= \varrho_1\frac{\partial v_1}{\partial t} + s\,(v_1 - v_2) \\ -\frac{\partial p_2}{\partial x} &= \varrho_2\frac{\partial v_2}{\partial t} + s\,(v_2 - v_1) \end{aligned} \qquad (38)$$

where p_1 and p_2 are the forces per unit area of cross section exerted on the frame and on the air respectively, s is a coupling coefficient, taken at the same value in both equations because of the law of action and reaction For $v_1 = 0$, the second equation should become identical with formula 21, corrected for h and k', *cf* formula 34, so that

$$s = j\omega\,\frac{4}{3}\,\frac{k'-1}{h}\,\varrho_0 + \sigma \qquad (39)$$

s therefore is a function of frequency The equations of continuity are

$$\begin{aligned} -\frac{\partial p_1}{\partial t} &= K_1\frac{\partial v_1}{\partial x} \\ -\frac{\partial p_2}{\partial t} &= K_2\frac{\partial v_2}{\partial x} \end{aligned} \qquad (40)$$

After substituting $j\omega$ for $\partial/\partial t$ and γ for $-\partial/\partial x$, and after elimination of all p's and v's, an equation for the propagation constant is obtained

$$\left(\frac{\gamma}{j\omega}\right)^4 - \left(\frac{\gamma}{j\omega}\right)^2\left[\frac{\varrho_1 + s/j\omega}{K_1} + \frac{\varrho_2 + s/j\omega}{K_2}\right] + \frac{\varrho_1\varrho_2 + (\varrho_1 + \varrho_2)s/j\omega}{K_1 K_2} = 0 \qquad (41)$$

the roots of which are $\pm\gamma'$ and $\pm\gamma''$ The $\pm$ sign relates to the two directions of propagation and in any direction two different values of γ may be found, that is two waves moving with different velocities This is not to be understood as indicating that the solid material is the carrier of one wave and the air the carrier of the other On the contrary both skeleton and air carry two waves Four wave impedances can be distinguished w_1' and w_1'' for the frame and w_2' and w_2'' for the air These wave impedances can be calculated from the equations of motion, the equations of continuity and from conditions at the layer boundaries

The behaviour of the system in general cannot be described in a few words, but it is possible to say something for the limiting cases of very tight and very loose coupling In the first, the material will behave as one with a density $\varrho_1 + \varrho_2$ and a bulk modulus $K_1 + K_2$ and the absorption characteristic will not differ substantially from those spoken of in the last sections However, loose coupling is more interesting Now one of the waves, say γ'', may be considered as the modified air wave and the second γ' as the modified skeleton wave The material behaves as consisting of two impedances, in parallel if the front surface is open, and in series if the front surface is closed by a light and impervious membrane

Of these two again only one is interesting, namely the one with the closed surface The skeleton of a material with open front surface will hardly be influenced by the incident sound waves because of the small area that is exposed Such a material with slight coupling will therefore behave scarcely differently from the corresponding material with rigid skeleton With a closed front surface however the frame will have to bear a considerable part of the external load and it will have an opportunity to be set into vibration Because of the differences in the two γ's the skeleton wave and the air wave will help each other at certain frequencies and at other frequencies counteract each other, thus producing exceedingly low total impedances for certain frequencies, accompanied by exceedingly high sound absorption for these same frequencies The absorption characteristic now no longer shows the continuous rise of *Figure 6*, but pronounced resonances may be shown *Figure 7* shows the influence of

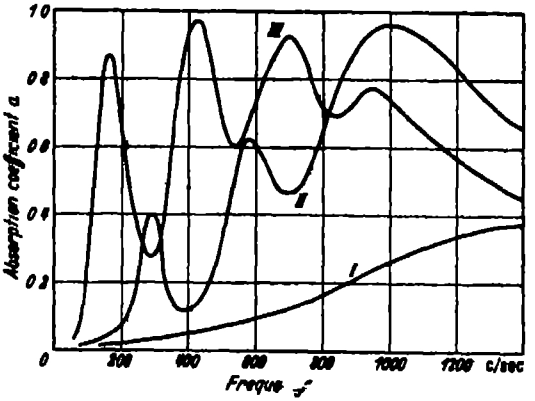

Figure 7 Absorption characteristics of Latucel, a sponge rubber material I with open front surface II coated with a layer of cellophane, 0 1 kg/m² III coated and mounted on perforated sheet iron plate, 78 mm from wall

closing the front surface These measurements were performed on a sponge rubber called *Latucel* of specific flow resistance 20 c g s units, the cover consisted of a layer of cellophane of 0 1 kg/m²

For materials like *Latucel* the enclosed air is stiffer than the rubber skeleton and it is possible to make them more alike by backing the material with a layer of air Better compensation of the impedances can now be anticipated, resulting in very high absorption at low frequencies, see *Figure 7* To get rid of the sharp peaks one may apply materials of inhomogeneous composition or use inhomogeneous mounting [8]

CONCLUSIONS

The author hopes to have made clear that sufficient knowledge of the fundamentals of sound absorption is available to enable engineers to develop adequate materials

A problem left open for future research is the correlation of sound absorption as measured by reverberation methods with the data obtained from interferometer methods

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Applications of Amalgam Metallurgy

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Amalgam metallurgy was reviewed as a new concept in a previous article[1] which showed how the techniques associated with it were devised and which then outlined the most important properties of amalgams from a technological standpoint, the affinity of metals for mercury being one of the chief features

It is useful to divide amalgams into three groups according to their technical applicability, which can be designated by naming for every group one characteristic metal as the iron, zinc and sodium types This division corresponds to three different degrees of affinity with mercury, and it is striking that the metals having good solubility in mercury occupy places next to mercury in the periodic table, both horizontally and vertically, this indicates a correlation between miscibility and the structure of the outer electron shells, *Figure 1* It should be noted here that the amalgam technique in metallurgy is concerned almost entirely with easily flowing amalgams, either true solutions of metals in mercury or very dilute amalgam sludges which in outward appearance and flow properties are scarcely distinguishable from pure mercury the metals are handled in the flowing state at room temperature

Various selected techniques will now be reviewed in turn

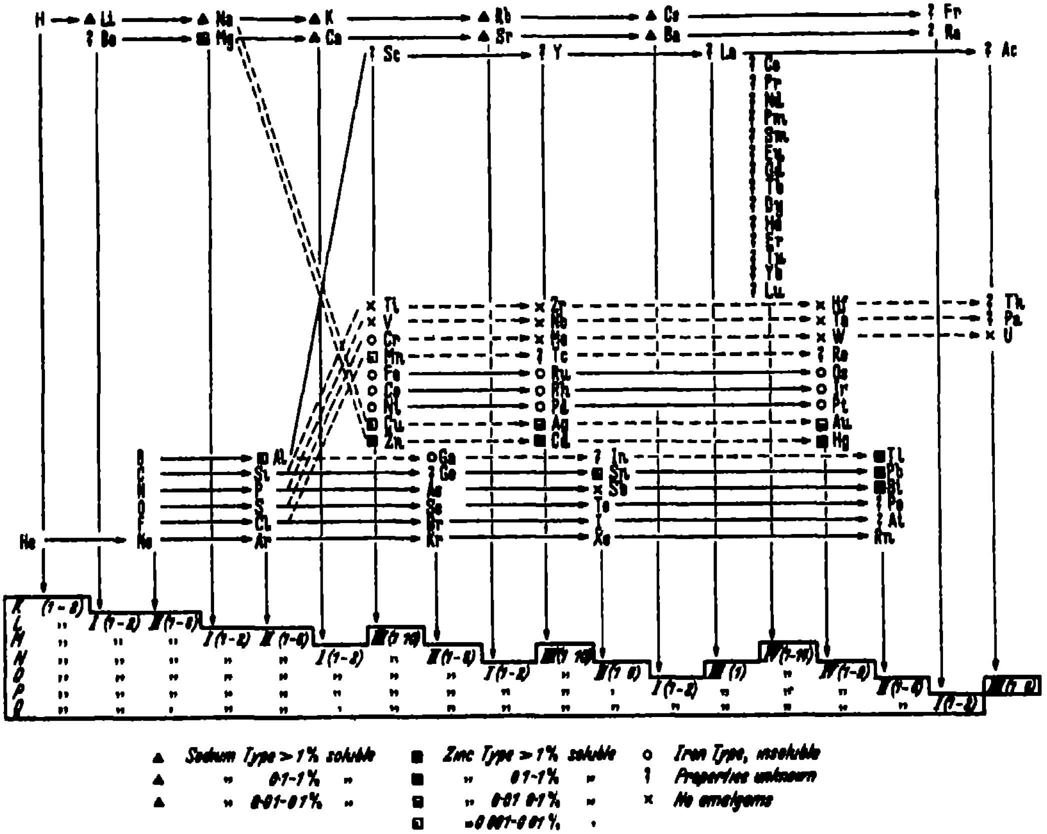

Figure 1 Amalgam formation in relation to the periodic classification of elements

TECHNIQUES BASED ON PROPERTIES OF THE AMALGAM

Example of a filtration process : extraction of aluminium from* ' AlFeSi '— Separation methods based on differences of solubility, such as filtration, decantation and the like, are amongst the most usual and important operations of industrial chemistry The only methods of a similar nature used in metallurgy are the crude methods of refining metals like the separation of silver from copper which have a low separating power Separation of metallic systems by means of filtration is, on the contrary, so unusual and so utterly alien to the metallurgist that I J. FOUNDAMINSKY and H LOEVENSTEIN, who were perhaps the first to conceive the principle of applying filtration methods to metallurgy, have patented it[8]; among other possibilities they proposed the use of molten lead, molten zinc and mercury as solvents for the extraction by selective dissolution of individual metallic components from metallic systems.

During the 1939–45 war these ideas were taken up by the Eula Works in Saxony (Walter Schmidt) and by the I G Farbenindustrie A G at Bitterfield (Messner) with the aim of developing a low energy consuming process of aluminium extraction The raw materials were either light metal scrap (available in large quantities from shot-down aircraft) or the so-called ' AlFeSi ', an alumino-ferro-silicon obtained by thermal reduction of certain aluminous silicates in a similar manner to ferro-silicon The process is based on the considerable solubility of aluminium in mercury at high temperatures and the insolubility of iron and silicon On cooling, aluminium crystallizes out, being practically insoluble in mercury at low temperatures The filtration is therefore double, once at high temperature and once again at low temperature, resulting in a high degree of separation and purity

The solubility of aluminium in mercury only begins to be appreciable at temperatures well above the boiling point of mercury under atmospheric pressure (solubility 0·001 per cent at 25°C, 0·17 per

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* The author has no personal practical experience of the first two processes described.

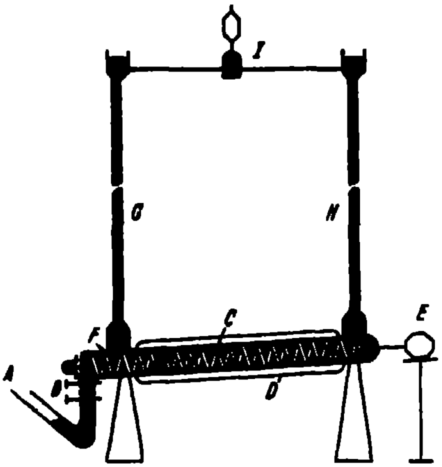

Figure 2 Extraction of aluminium from mercury under pressure A intake, B double pressure lock, C tubular screw conveyor, D heating jacket, E conveyor motor, F ceramic filter, G ascending tube, H descending tube, I mercury pump

cent at 300°C, 10 per cent at 550°C) It is therefore necessary to operate at high pressure *Figure 2* shows schematically an apparatus devised by G. MESSNER The necessary pressure of 15 atm is obtained by using two upright tubes each 12 m high in which the mercury circulates, ascending in one and descending in the other The raw material enters at low level through a pressure lock It is borne by a screw conveyor against a stream of superheated mercury coming from the descending tube At the bottom of the ascending tube there is a ceramic filter preventing the passage of insoluble materials, the dissolved aluminium crystallizes out as the ascending mercury cools, and floats on the surface of the mercury in the container at the top of the ascending tube where it is collected The bottom of the descending tube has no filter and the insoluble components being lighter than mercury rise against the current and float on the surface of the mercury in the container at the top of the descending tube, where they are collected

The main attraction of this and similar methods lies in the low energy consumption The extremely high energy consumption of the usual electrolytic methods of aluminium extraction, using a molten electrolyte, is the main problem of the aluminium industry, at least in Central Europe In spite of the building of new thermal and hydraulic power stations the energy demand increases more rapidly than the supply Aluminium works require a particularly heavy capital outlay, 1,000 gold marks per ton of yearly production as compared with 60 to 100 gold marks per ton for carbide works or with 20 gold marks per ton for superphosphate works A particular disadvantage, therefore, is that they can frequently only be operated in summer when supply is abundant and have to close down in winter due to lack of energy

Energy consumption in the usual molten electrolyte process is about 20 kwh per 1 kg of aluminium, but experience gained at Bitterfield would indicate an energy consumption of 0 9 kwh plus 2 7 m^3 of generator gas per 1 kg of aluminium, this is obviously of very great importance It should, however, be mentioned that the process has not yet gone beyond the experimental stage The greatest and, perhaps, a decisive difficulty, at least for 'AlFeSi', is that a considerable proportion of the aluminium forms alloys with the components which are insoluble in mercury and so does not take part in the process

Extraction of metallic sodium, a special case of the alkali chloride electrolysis process— Many attempts have been made, especially in the U S A, to replace the Downs process of sodium extraction, which presents considerable difficulties, by a process based on the use of mercury During 1939–45 similar experiments were made in Germany in a smaller plant of the I G group in Bavaria

The Downs process[3] is an electrolysis of molten sodium chloride and therefore operates at very high temperatures Like all molten electrolyte processes it has a much higher energy consumption (14 to 16 kwh per 1 kg sodium) than the aqueous electrolytic processes Owing to the exceptionally high under voltage of sodium at a mercury cathode it is easily possible to extract metallic sodium, which otherwise reacts with water, from an aqueous solution on to a mercury cathode (4 5 kwh/kg sodium) and this process has long been in use industrially in the form of the mercury-cathode electrolysis, the electrolyte being a sodium chloride solution But while it is comparatively easy to break down the sodium amalgam by means of water and a graphite catalyst into sodium hydroxide solution and hydrogen gas, as is done in that process, it is technically much more difficult to extract metallic sodium from the sodium amalgam

This extraction has been attempted by two different processes, both typical amalgam metallurgy techniques One process is based on the removal of mercury by thermal distillation The other is based on an electrolysis in an auxiliary electrolyte of molten salt which is not used up, the sodium being transferred from the amalgam on to a solid cathode on which it is deposited in molten metallic form

In favour of distillation is the fact that iron is not attacked either by hot mercury or by hot sodium i e iron distilling apparatus can therefore be used The separation is, however, difficult because even at a temperature at which sodium begins to evaporate it is not entirely free from mercury A displacement process is therefore used, displacing sodium from the amalgam by metallic calcium which has an even greater affinity for mercury than sodium (see ref 1 *Figure 1*) and displaces the sodium without mixing with it even at high temperatures Owing to its high boiling point, calcium can easily be recovered by distillation of the mercury

The anodic transfer electrolysis makes use of a molten electrolyte with the lowest possible melting point *e g* sodium bromide-sodium hydroxide, m pt 260°C As with all electrolytic processes using a soluble anode, the energy consumption is low The metallic sodium is deposited on an iron wire net cathode and rises to the surface, the sodium amalgam has a very high specific weight and stays at the bottom of the cell, below the molten electrolyte The metallic sodium is removed from time to time

Amalgam electrolytic processes using molten electrolytes may also become important for the extraction of aluminium , aluminium amalgam is immediately decomposed by water and so electrolysis in aqueous solution is not available A few years ago laboratory experiments were made on these lines at the I G works at Leverkusen, using the sodium chloride-aluminium chloride mixture which has an exceptionally low melting point

Example of semi-electrolysis processing zinc alloy scrap—The recovery of various metals from scrap is often of great importance For example, for aluminium the quantities of metal recovered from scrap amount to about one fourth of the total supply, and for tin and lead to about one third For iron, particularly in countries like Italy and Japan which have little coal, regenerated metal may amount to as much as one half of the total consumption In war time or after catastrophes the scrap cycle increases considerably in volume so that the quantities of regenerated metals may be equal to or even greater than the quantities of new metals extracted from ore

Regenerated metal obtained from melted down scrap is always cheaper and of poorer quality than new metal obtained from ore because its impurity content is higher and more irregular It is for this reason that the scrap cycle of zinc alloys is only about 10 per cent of the total volume. Owing to the development of spray casting, for which these alloys are particularly well suited, the low volume of the scrap cycle presents a serious problem for the metal industry The alloys used for spray casting consist of a base of purest electrolytic zinc and 1 to 15 per cent, usually about 4 per cent, of aluminium and 0 3 to 4 5 per cent, usually about 4 per cent, of copper, but they must be absolutely free from certain impurities which are often unavoidably introduced with melted down scrap

Amalgam metallurgy made it possible to develop a very simple and economical process for obtaining purest zinc and the admixture metals, separated and in a readily usable form, starting from scrap alloy The scrap is degreased and then dissolved in mercury in the presence of dilute sulphuric acid The aluminium contained in the scrap alloy reacts with the water and is finally recovered in the form of pure aluminium sulphate crystals , the other alloy metals do not react with the water The iron and copper contained in the alloy are not dissolved in mercury and can be separated from the liquid zinc amalgam by filtration , they are obtained in the form of iron-zinc amalgam and copper-zinc amalgam The former is magnetic in spite of its high zinc content and sometimes the two can be fairly completely separated by magnetic means , the alloys are obtained in powder form by the distillation of mercury The less reactive accompanying metals, such as tin, lead and cadmium, are gradually accumulated in the zinc amalgam The zinc is obtained by electrolysis in a pure acid zinc sulphate solution which is not used up, the amalgam being the anode The cathodes are of aluminium The deposited zinc is of 99 999 per cent purity

Figure 3 shows the cell used in this process, which is a further development by E Kuss, Duisburg, of the vertical cell devised by W Honsberg of Ludwigshafen The main features of this cell are the slowly revolving iron disks of 2 m diameter, plunged half into the amalgam pool and half into the electrolyte Passing through the amalgam the disks are amalgamated and this gives to the anodic amalgam the vertical position necessitated by the vertical cathodes This is an elegant solution of an important problem

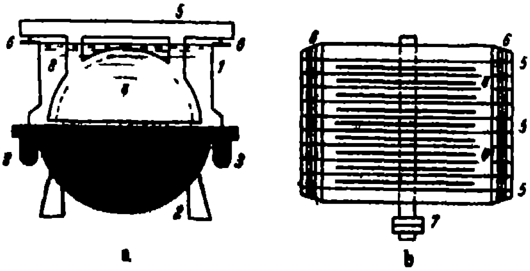

Figure 3 Anodic cell a cross section, b plan, 1 trough, 2 amalgam pool, 3 air tight plunging lock (siphon), 4 anode disks, 5 cathode plates, 6 power intake, 7 rotation shaft, 8 electrolyte

of amalgam metallurgy The circulation of the amalgam between the scrap dissolving pool and the anodic cell, the speed of revolution of the anode disks and the current intensity per unit area, must be determined in such a way that a relatively small proportion of the zinc (the zinc content of the amalgam should decrease for instance from 2 2 to 2 0 per cent) is removed from the amalgam in the anodic cell while it must be constantly replenished from the dissolving pool Here, owing to the third law of amalgam potentials[1], the accompanying alloy metals which had passed into the amalgam (tin, lead, cadmium *etc*) do not pass into the electrolyte even as traces This automatically ensures the exceptionally high purity of the zinc even if a high proportion of accompanying alloy metals has accumulated in the amalgam

The half wave potential of zinc amalgam having practically the same value as the normal electrode potential of zinc (see *Table I*, and ref 1 *Figure 2*), there is no fall of voltage to overcome at the electrodes This leaves only the slight electrolytic resistance of the electrolyte itself, which is a good conductor, so that the cell voltage is of the order of 0 4 v only The energy consumption is about 0 35 kwh/kg zinc *i e* about one ninth of the consumption usually needed for electrolytic zinc Contrary to other amalgam electrolysis processes, the amalgam here is not obtained by means of electrolysis and so the process may be called an amalgam-metallurgical semi-electrolysis It is scarcely necessary to mention that electrolytic refining without mercury *e g* with solid anodes made of melted down scrap, is entirely excluded because of the disagreeable effect of impurities contained in the raw material

Table I Polarographic Half Wave Potentials and Maximum Molar Amalgam Formation Energies of Metals at Room Temperature

Metal	E_n volt	$E_{\frac{1}{2}}$ volt	$\frac{0\ 058}{n}\log\left(\frac{1\ 000\rho}{M}-1\right)-\varepsilon$	$-E_n+E_{\frac{1}{2}}+\varepsilon=\Delta F$	$2\ 89\times10^{4}\ n\ F\ \Delta E$ kcal
Co	− 0 58	− 1 23	0 08$_8$	0 71$_2$	32 9
Fe	− 0 73	− 1 33	0 06$_8$	0 66$_8$	30 6
Ni	− 0 51	− 1 10	0 06$_8$	0 65$_8$	30 2
Cr	− 0 85	− 1 42	0 08$_1$	0 69$_1$	29 1
Mn	− 1 39	− 1 55	0 08$_1$	0 22$_1$	10 2
Pb	− 0 41	− 0 46	0 05	0 10	4 6
Sn	− 0 43	− 0 47	0 04$_9$	0 08$_9$	4 1
Zn	− 1 06	− 1 05	0 05$_9$	0 04$_9$	2 2
Cd	− 0 69	− 0 65	0 05$_4$	0 00$_6$	− 0 3
Tl	− 0 63	− 0 50	0 10$_8$	− 0 02$_8$	− 0 5
Bi	− 0 09	− 0 05	0 03$_8$	− 0 09$_8$	− 1 9
Na	− 3 00	− 2 15	0 09$_8$	− 0 75$_7$	− 17 4
Li	− 3 25	− 2 32	0 10$_9$	− 0 82$_1$	− 18 9
K	− 3 21	− 2 18	0 07$_7$	− 0 95$_9$	− 22 0
Sr	− 2 79	− 2 14	0 04$_8$	− 0 60$_9$	28 1
Ca	− 3 16	− 2 24	0 04$_6$	− 0 87$_4$	− 40 4
Ba	− 3 09	− 1 95	0 05$_7$	− 1 10$_9$	− 50 8

n = valency, F = 96 540 coulomb, M = molecular weight, ρ = density, E_n = normal electrode potential, $E_{\frac{1}{2}}$ = half wave electrode potential

Example of blocking electrolysis extraction of zinc of 99 999 per cent purity from the purple ore— The zinc-containing lyes finally obtained in the chlorinating calcination process cannot be electrolysed by the usual methods for three reasons they are chlorides, they have a high impurity content and they are neutral Although many efforts had originally been made to develop methods for the electrolysis of zinc chlorides (Höpfner), the sulphate electrolysis processes finally predominated The advantage of chloride electrolysis is the lower potential difference in the cell , the main disadvantage is the necessity of using diaphragms The anodic part of the cell must be air tight because of the chlorine gas while the cathodic part must be kept open because the cathodes must be removed periodically The two parts must therefore be separated by a diaphragm

The electrolyte used in zinc electrolysis must be very pure if the consumption of energy is to be kept within economic limits Traces of metallic impurities result in the formation of local cell elements and therefore in an increasingly rapid re dissolution of the deposited zinc Because of the ability of molten pyrites to dissolve many elements, the lyes of the chlorinating calcination process always contain a considerable amount of impurities and satellite metals, making a high degree purification very difficult and expensive

Finally, the zinc deposited in the electrolysis of alkaline, neutral or even of feeble acid solutions is obtained in a technically worthless spongy form, so that it is necessary to work with fairly acid solutions To make the chlorinating calcination process lyes sufficiently acid would also be expensive because it would entail adding hydrochloric acid which is alien to the main process and must be bought

In order to extract zinc of electrolytic purity from these lyes by the usual techniques it would therefore be necessary to proceed first to a preliminary purification of the solution, then to precipitation with lime, then to drying completely the zinc hydrate thus obtained (otherwise the electrolyte which is used in a closed circuit would be increasingly diluted) and to dissolving it in an exhausted *i e* poor in zinc and strongly acid, zinc sulphate electrolyte solution, then to dechlorinating this solution completely *e g* by

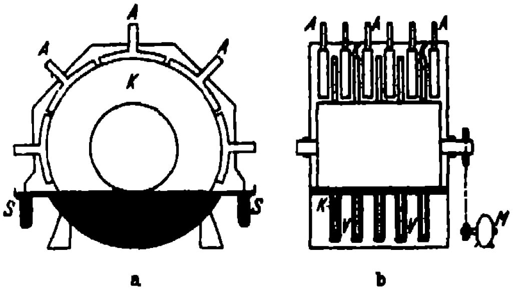

Figure 4 *Messner cell* a *longitudinal section*, b *cross section*, *A graphite anodes*, *K cathode disks*, *V plungers*, *M motor*, *S siphon*

means of silver sulphate (it is impossible to wash zinc hydrate entirely free of chloride owing to the formation of zinc oxychloride), and finally to achieving a high degree of purification prior to electrolysing it Such a chain of technical processes is much too expensive for a relatively common product such as electrolytic zinc

Amalgam metallurgy opens an entirely new way The lyes of the chlorinating calcination process can be electrolysed as they are *i e* as a neutral zinc chloride solution with a very high impurity content, the zinc being transferred as zinc amalgam on to mercury cathodes The cells used in this process are the highly developed and very efficient cells of the chlorine-alkali electrolysis process *Figure 4* shows an interesting construction of such a cell, the Messner cell The slowly rotating cathodes are in the form of circular rings and not full disks as in the cell shown in *Figure 3* The mercury pool is therefore smaller and requires less mercury , mercury being expensive, this is an advantage To compensate for the loss of surface in the electrolyte the mercury pool is placed at a lower level, so that the greater part of the ring is bathed in the electrolyte

The cell is air tight The fluid zinc amalgam leaves the cell through a siphon lock and is obtained free of electrolyte and chlorine gas As the anodic chlorine gas may either be sold as such, at a substantial profit, or be used in the main chlorinating process, it is an asset instead of the liability it is with the Höpfner process The approximately neutral reaction of the electrolyte does not interfere with the formation of the cathodic amalgam

The behaviour of the metallic impurities contained in the lyes is particularly interesting Those that are more reactive than zinc *i e* have a greater negative half wave potential (see *Table I* and ref 1 *Figure 1*) do not pass into the amalgam and are evacuated with the exhausted lyes The impurities which are less reactive than zinc pass with it into the amalgam, but by virtue of the first amalgam potential law[1] they cannot form local cell elements which would lower the efficiency of the process by increasing the consumption of energy Amalgam metallurgy thus creates an unprecedented situation for aqueous electrolysis processes by making it possible to electrolyse low grade cheap metallic saline solutions with a high impurity content just as readily and efficiently as the very pure, sensitive and expensive electrolytes of the usual solid cathode processes (Anaconda, Tainton, Giesche)

The fluid amalgam circulates in a continuous closed circuit passing from the cathodic amalgam cell through the siphon into an anodic amalgam cell and finally back to the cathodic cell, *Figure 5* The anodic cell operates with an extremely pure stationary acid zinc sulphate electrolyte which is not used up and has aluminium cathodes Provided the zinc concentration of the amalgam is lowered only slightly, the operation of the third amalgam potential law[1] ensures that only the zinc leaves the amalgam and is deposited on the cathodes with a 99 999 per cent purity , the less reactive accompanying metals remain in the amalgam where their concentration increases progressively It is thus possible to extract, from an aqueous solution with a high impurity content and without going through a separate purification process, a zinc of a higher degree of purity than that usually obtained from the purest electrolytes The mercury, serving as an intermediate phase, acts as an automatic and universal impurity block of the highest efficiency This form of amalgam electrolysis may therefore be called a blocking electrolysis

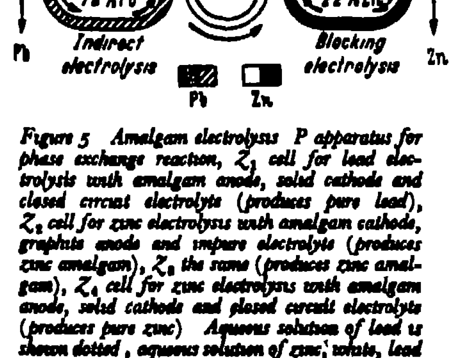
Aqueous solution of lead and zinc salts
P
Cl_2
Exhausted solution
18%Pb
25%Zn
Z_1 Closed Z_2 amalgam circuit
Z_3 Closed Z_4 amalgam circuit
12%Pb
22%Zn
+
+
−
−
Pb
Indirect electrolysis
Blocking electrolysis
Zn
Pb
Zn

Figure 5 *Amalgam electrolysis* *P apparatus for phase exchange reaction*, Z_1 *cell for lead electrolysis with amalgam anode, solid cathode and closed circuit electrolyte* (*produces pure lead*), Z_2 *cell for zinc electrolysis with amalgam cathode, graphite anode and impure electrolyte* (*produces zinc amalgam*), Z_3 *the same* (*produces zinc amalgam*), Z_4 *cell for zinc electrolysis with amalgam anode, solid cathode and closed circuit electrolyte* (*produces pure zinc*) *Aqueous solution of lead is shown dotted , aqueous solution of zinc, white, lead amalgam, hatched, zinc amalgam, black*

The efficiency of the purifying effect of this blocking electrolysis can be assessed by making use of the previously mentioned amalgam potential laws Considering first the metals which are more reactive than zinc, let us assume that the lyes contain cobalt, iron and manganese, having respective half wave potentials 0 17 v, 0·27 v and 0 49 v lower than that of zinc, in a concentration equal to 0 1 of the zinc for each According to the amalgam potential formulae, the content in these metals of the 2 per cent zinc amalgam will be 3 × 10^{-7} per cent cobalt, 2 × 10^{-10} per cent iron and 3 × 10^{-18} per cent manganese Considering now the metals which are less reactive than zinc, let us assume that the zinc is accompanied by cadmium, thallium and tin, with respective half wave potentials 0 43 v, 0 56 v and 0 59 v higher than that of zinc, and the concentration of which in the amalgam gradually increases to 0 2 per cent each *i e* also 0 1 of the zinc content According to the amalgam potential formulae, the equilibrium concentrations of these metals in the pure 2N zinc sulphate electrolyte of the anodic cell will be 2 × 10^{-10} gm/l for thallium, 1 × 10^{-16} gm/l for cadmium and 4 × 10^{-21} gm/l for tin Thus the more reactive metals are retained in the original aqueous solution whilst the less reactive metals are retained in the amalgam

As has already been mentioned, the potential difference of the anodic amalgam cell is very low The potential difference of a chloride cell is lower than that of a sulphate cell The blocking electrolysis, despite the fact that it works with two cells, therefore consumes no more energy than the usual single cell zinc sulphate electrolysis The chlorine gas, which is obtained as a by-product, is necessary for the main chlorinating process and would otherwise have to be produced by a chlorine-alkali electrolysis Deducting the amount of energy corresponding to that process, the net energy consumption for the extraction of zinc by the amalgam process is seen to be considerably lower than that of the usual electrolytic processes Working with a low grade raw material, the process is also considerably cheaper

Example of indirect amalgam electrolysis extraction of electrolytic lead from low grade zinc ores— Whereas the electrolytic extraction of many metals, such as copper, zinc or cadmium, from their saline solutions is a relatively easy matter, with other metals this is by no means true. For example, not only does the electrolytic extraction of manganese require an exceptionally pure electrolyte (the specific energy consumption and the density of the electrolytic manganese deposit is a much more sensitive purity criterion of the electrolyte than the most sensitive analytical methods) but there is also an anodic precipitation of manganese in the form of hydrated manganese dioxide which complicates the process very considerably from the technical and industrial points of view Finally, in order to prevent a re-dissolution of the cathodic manganese deposits by the acid formed at the anode, the cell must be divided by thick diaphragms, costly in themselves and increasing the energy consumption.

With lead, the anodic precipitation of lead dioxide has been an important factor preventing the development of a process for the direct extraction of electrolytic lead from lead ore The most important reason, however, why no electrolytic process could be developed is that the more easily soluble lead salts, such as the perchlorate or the hydrosilicofluoride, are much too expensive for ore processing whereas the more common salts, such as lead chloride, are too insoluble to permit use of the high current densities which are necessary for the economic operation of an electrolytic process

The anionic level of a metallic salt solution can also be a hindrance to its electrolysis as the common anode materials are usually resistant to one kind of anion only For example, lead anodes—especially if, according to U C TAINTON's invention, they contain 0 5 per cent silver—have an excellent resistance to a sulphate ion discharge,, but they are corroded by nascent chlorine The chlorine-resistant graphite anodes, on the other hand, are rapidly oxidized by the nascent oxygen liberated by the electrolysis of sulphate solutions

It should be mentioned in this context that the various more or less reactive anions behave in a manner comparable to that of the more or less reactive cations, as these last are more or less easily deposited on the cathode, so the anions are more or less easily oxidized on the anode Depending on the material of the anode and on the extent to which it can be oxidized, the various anions are precipitated at different anodic potentials, the nitrate ion less easily than the sulphate ion, this less easily than the chloride ion, or the hydroxyl, cyanide and sulphide ions in that order It may therefore be possible to electrolyse a sulphate-containing chloride electrolyte within certain limits of concentration and of current density per unit area without liberation of oxygen and therefore without damage to the graphite anodes On the contrary, it is not possible to electrolyse a chloride-containing sulphate electrolyte, as even a very low concentration of chloride ion leads to the destruction of the lead anodes used in sulphate electrolysis It is for the same reason that the electrolysis of a zinc chloride solution requires less energy than that of a zinc sulphate solution , the potential difference is smaller in a chloride electrolysis because a copper cell requires a lower potential difference than a zinc cell

When a low grade lead-zinc ore is processed by chlorination followed by leaching, the zinc chloride is dissolved first The lead chloride is nearly insoluble in a concentrated zinc chloride solution, it is therefore dissolved only after the greater part of the zinc chloride has been removed from the solution The low concentration of the lead chloride and the formation of lead dioxide on the anode makes it impossible to electrolyse these solutions by the ordinary process of aqueous electrolysis *i e* using solid cathodes The techniques of amalgam metallurgy, however, permit an easy solution of this problem

The process, shown schematically in *Figure 5*, is primed by zinc amalgam The lead chloride solution is not electrolysed directly Instead it is brought into intimate contact with the zinc amalgam Owing to the operation of the second amalgam potential law *i e* because the affinity of lead ions for electrons is greater than that of zinc ions, an exchange between the two phases—the aqueous solution and the amalgam—takes place across their surface of contact, the lead passing from the solution into the amalgam and replacing the zinc which passes into the solution This process is obviously exempt from the previously mentioned difficulties, there is no disturbing anodic reaction and the exchange does not depend on the conductivity of the lead chloride solution which is too low for ordinary electrolysis The solution from which the lead content has thus been extracted passes on to two consecutive electrolysis cells with mercury cathodes, the first serves to replenish the zinc content of the amalgam used for the lead extraction, the second totally to extract zinc from the aqueous solution in the form of zinc amalgam from which the zinc is then extracted in metallic form in a third cell by the blocking electrolysis described The lead is also extracted in metallic form from its amalgam by a blocking electrolysis in a fourth cell using a lead salt electrolyte of high purity and high conductivity which is not consumed

The electrolysis is thus indirect, the aqueous electrolysis operating with the readily electrolysed zinc chloride solution instead of the lead chloride solution which is difficult to electrolyse The process presents all the advantages of blocking electrolysis and the lead is obtained in a state of spectroscopic purity The phase exchange reaction is almost instantaneous if the phase contact area is made sufficiently large and if the contact zone is strongly agitated

The market price of lead is about the same as that of zinc, while its equivalent weight is three times greater The direct extraction of electrolytic lead from low grade ore is therefore industrially an even more advantageous process than the extraction of zinc

Example of a concentration transforming process extraction of rare zinc satellites— A constant zinc satellite is cadmium, usually met with in a concentration of about 0 1 per cent Indium and gallium are also frequently present in zinc ores, though in very small quantities, sometimes *e g* in the Meggen ore, thallium is also to be found In the usual zinc sulphate electrolytic processes these metals accumulate in the cementation sludge which is precipitated when the electrolyte is periodically purified by zinc powder The corresponding operation in amalgam metallurgy consists in bringing the aqueous solution into intimate contact with the zinc amalgam prior to the electrolysis proper, a phase exchange occurs in which, owing to the operation of the second amalgam potential law, the rare earths displace the zinc from the amalgam and accumulate in it

Compared with the cementation by zinc powder, the phase exchange process presents the disadvantage that gallium is lost, owing to its high potential with respect to mercury it cannot be recovered from the amalgam On the other hand it presents the advantage that, as long as the aqueous solution contains no atmospheric oxygen or other oxidizing substance which can corrode the amalgam, the phase exchange occurs stoichiometrically, the subsequent decomposition of the multi-metal amalgam obtained can be fractionated very sharply, the zinc satellites being obtained in the form of very pure and concentrated solutions In the cementation by zinc powder used in the aqueous electrolysis, the cementation agent *i e* zinc, must be used to excess, sometimes up to 25 times that of the stoichiometrically required quantity, and the processing of the complex cementate, containing large amounts of zinc, is complicated and expensive

Provided the phase contact area, mercury/water, is sufficiently large and the zone of contact sufficiently agitated, the phase exchange of zinc with the satellite traces is very rapid and the process may therefore be continuous, operating with a constant flow of aqueous solution A large contact area and the necessary agitation can be achieved by dispersing the amalgam in the water in the form of fine droplets, this can be done either in a paddle washer or in an apparatus, such as that shown in *Figure 6*, provided with conical flinging basins with open bottoms having a high speed of revolution and dipping into a small pool of amalgam

A good method for the decomposition of the multi-metal amalgam thus obtained, and therefore also for the periodical purification of the amalgam used in closed circuit processes such as the blocking electrolysis, is oxidation by means of nitric acid. Nitric acid attacks all amalgams very rapidly and has the

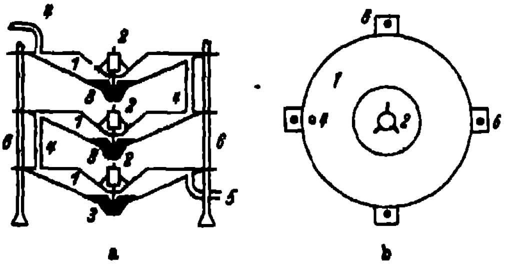

Figure 6 Flinging apparatus for phase exchange a *cross section*, b *plan*, *1 reaction trough*, *2 motor*, *3 amalgam-flinging basin with amalgam pool*, *4 piping for solution*, *5 solution exit*, *6 supports*

further advantage that all its salts are easily soluble Another good method is phase exchange with a suitable mercury salt *e g* mercury chloride which is easy to prepare from mercury and chlorine gas , the mercury enters the amalgam and displaces the metals contained in it

The metals contained in the amalgam are always obtained in the same concentration as that of the decomposing agent which is used It can therefore be said that, in the process of extracting metals from highly diluted solutions, the mercury phase functions in the manner of a concentration transformer This method of concentration can naturally be employed not only for the extraction of zinc satellites, such as cadmium, indium and thallium, or of lead satellites, such as silver and bismuth, but also for the processing of various other exhausted or dilute solutions obtained in mining and metallurgical processes

Example of a continuous process for separation of multimetallic mixtures by means of a progressive phase exchange based on complex potentials the alkaline processing of rotary kiln oxides — The purifying efficiency of amalgam metallurgical separation processes, such as the blocking electrolysis and the phase exchange processes, is based on a sufficiently wide dispersion of the half wave potentials of the metals to be separated As can be seen from *Table I*, and ref 1 *Figure 2*, this is not always so In complex-forming solutions however (alkaline solutions of ammonium salts, caustic soda solutions, cyanide solutions, tartrate solutions) the half wave potentials of metals are increased (become more strongly negative) and this effect can be of very different magnitude for different metals, see *Table II* It is therefore frequently possible to realize by means of complex potentials separations which would otherwise be impossible

Rotary kiln roasting is a process used for the ores of relatively volatile metals The ore is heated somewhat below its melting point in a rotary kiln with a reducing atmosphere The metals escape from the ore in a gaseous state and are later oxidized and so precipitated by atmospheric air introduced near the further end of the kiln These so-called ‘ rotary kiln ’ oxides are mixed with a considerable amount of dust , they may contain, for example, approximately equal parts of lead oxide, tin oxide and zinc oxide The half wave potentials of lead, tin and zinc with respect to the normal calomel electrode are – 0 46 v, – 0 47 v and – 1 06 v respectively It follows that if these oxides were dissolved in an appropriate acid, the separation of lead from tin would be impossible

In an alkaline solution, however, all three metals form ambivalent hydroxides, and their complex half wave potentials are – 0 81 v, – 1 18 v and – 1 41 v for lead, tin and zinc respectively It is therefore possible to separate the three metals by means of a phase exchange if their oxides are dissolved in a caustic soda solution *Figure 7* shows the apparatus used for a continuous process of this kind The alkaline solution of the metallic salts circulates inside a revolving drum divided by transverse partitions into many narrow chambers , the partitions are so arranged that the solution is forced to change direction at every partition, flowing inwards in one chamber and outwards in the next The other phase is zinc amalgam which is contained in small chambers on the periphery of the drum These amalgam chambers are separated from the inner part of the drum by porous partitions The amalgam contained

Table II Increase in Negative Value of Half Wave Potentials on Formation of Complexes in Solutions (values stated in mv)

Metal / Solution	Ni	Cu	Bi	Cd	Zn	Pb	In	Sn	Tl
Tartrate	—	130	350	—	—	—		—	0
Caustic soda	—	—	—	170	345	355	495	710	0
Cyanide	335	1,000	—	—	—	—	—	—	0

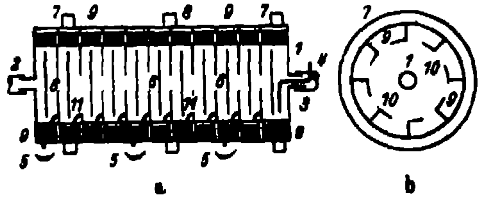

Figure 7 Rotary drum for fractionated phase exchange a *longitudinal section*, b *cross section*, *1 rotary drum*, *2 solution intake*, *3 solution exit*, *4 amalgam intake*, *5 amalgam exits*, *6 transverse partitions*, *7 ring bearings*, *8 gears*, *9 amalgam chambers*, *10 porous partitions*, *11 overflow pipes for amalgam*

in a chamber which is brought to the top by the rotation of the drum percolates through the porous partition, falls through the aqueous solution in the form of minute droplets and collects at the bottom where it percolates again through the porous partition and back into an amalgam chamber which for the moment is at the bottom Suitably disposed overflow pipes between consecutive amalgam chambers ensure a slow circulation of amalgam along the drum in the opposite direction to that of the aqueous solution

The amalgam is introduced at one end of the drum (the exit end for the solution) as pure zinc amalgam Part of it is continuously removed near the middle of the drum as pure tin amalgam and the rest is continuously removed at the far end as pure lead amalgam , these two amalgams are then processed separately for the extraction of tin and lead The original plumbite-stannite-zincate solution introduced into the drum leaves it at the far end (the entrance end for the amalgam) as a pure zincate solution which can be electrolysed easily to obtain zinc amalgam and a caustic soda solution which can be used anew for the alkalinization of the rotary kiln oxides

Such a continuous separation process for three metals, which can moreover easily be made entirely automatic by means of valves governed by relays which can be activated by potential differences, could not have been achieved by previous techniques It should be mentioned that in the amalgam process the zinc is obtained in a pure and usable form whereas using solid cathodes, as in an alkaline electrolysis, the zinc would be obtained in a spongy state, technically worthless because it cannot be melted without oxidizing it

Example of dry evaporation process manufacture of pure manganese alloys— After iron, manganese is the most common heavy metal in the earth's crust , it is for example 25 times more common than zinc and 60 times more common than lead In spite of this fact, manganese plays in industry the role not of a metal but of a chemical agent Nearly the whole of the world production of manganese is used in the form of ferro-manganese, a very impure alloy containing iron and carbon, for the desoxidation of molten steel , the greater part of the manganese is again lost in the slags.

Two factors have up to now prevented industrial use of manganese as a metallic material first, the poor technological qualities of impure manganese (great brittleness, small resistance to corrosion) and secondly, the considerable technical difficulties encountered in the extraction of pure manganese , these difficulties can be assessed by the exceptionally heavy purity premium paid for manganese

In recent years there have been some new developments and some creative ideas in the domain of manganese technology which seem to promise the introduction of radical changes into this rather sterile field which has seen no changes for some centuries. The bold and ingenious work of J KOSTER and S M SHELTON[4] has made it possible to obtain, by means of a kind of specially refined zinc electrolysis, a manganese of a formerly unknown degree of purity and at an astonishingly low price On the other hand, R S DEAN *et alii*[5] have shown that alloys of pure electrolytic manganese possess excellent technological properties, such as a high resistance to corrosion, hardenability, fatigue and heat resistance, as well as some entirely specific and technically very valuable properties, as for example an extremely high ability to damp vibrations

For all its elegance, Shelton's manganese electrolysis is a very exacting and difficult process and is very delicate Moreover, manganese only has a technical value in the form of alloys Finally, the manganese alloys have high melting points and are therefore particularly well adapted to the techniques of powder metallurgy For all these reasons the amalgam metallurgical process, producing pure manganese alloys in powder form, is technically and industrially specially interesting

The process is an indirect electrolysis in which a sodium amalgam is used for a phase exchange with an aqueous multi-metal saline solution containing all the components of the desired manganese alloy in the right proportions The alloy is precipitated and removed from the amalgam circuit The mercury is removed by distillation in an oven, preferably a tubular oven with a hydrogen atmosphere[6], similar to the ovens used in powder metallurgy The alloy is obtained in powder form

It has been emphasized[1] that the problem of low grade ores is the most important and complex problem of the metal industry The above rather uncommon method of mixing alloy components in the stage of aqueous metal saline solutions is of particular importance with low grade ores

The process regenerates the chlorine, and chlorination is the cheapest and most effective means of selective processing of ores The metal saline solutions are obtained by simple percolation and so are the cheapest possible raw material for electrolysis. The distillation is a cheap and simple process and furnishes the alloy powder directly i e a half finished product suited for modern metallurgical techniques. The process thus eliminates a whole series of inter-

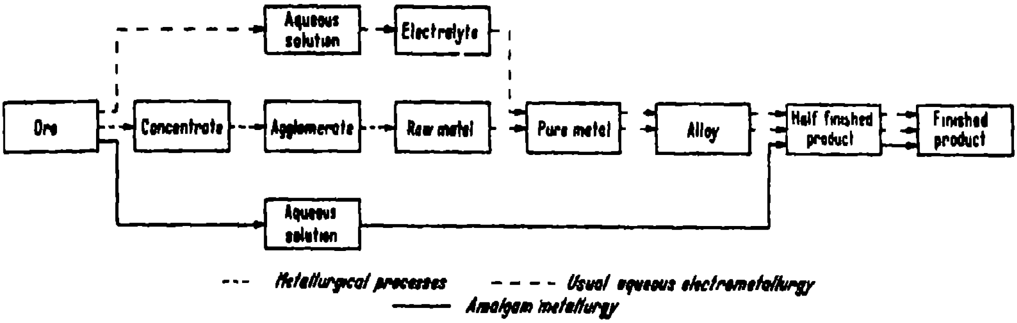

Figure 8 Production stages in the manufacture of metal products

mediary stages of the usual manufacturing processes, whether of metallurgical or of electrochemical nature (*Figure 8*) and this results in a considerable saving in cost The exceptional efficiency of the amalgam metallurgical process and the quality premiums it brings in make it possible to counterbalance the higher capital costs of low grade ore exploitation Even in its present early stage of development the process can supplement to a considerable degree the various processes working with higher grade ores although these are placed at a better economic advantage

The equipment and functioning of such an amalgam metallurgical alloy factory do not depend on the particular alloy produced, they remain the same whether the alloy happens to be a special manganese-based alloy with high vibration-damping properties, or a carbon-free chromium-nickel steel with an iron base, or a polish-taking cutlery alloy with a 'German silver' base, or a bearings metal, or any other combination of heavy metals with a high melting point This is obviously a further considerable advantage, making it possible to exploit, if necessary, a whole series of very different small low grade ore deposits simultaneously and/or to follow the movements of the metal market

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Photocopying Processes for the Research Worker

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A GREAT deal has been written on the broader subject of reproducing research materials It has already been well stated in the initial paragraph of R C BINKLEY's classic book[1] on this subject that 'The first duty of scholarship is to protect and preserve original writings, the loss of which would be irretrievable . Great importance must also be attached to those mechanical impediments which hinder a scholar whenever he is compelled to alter his plans or suspend his work because he can neither go to the material he needs nor have the material brought to him' It is particularly in overcoming these mechanical impediments that photocopying processes can be such an invaluable aid to research.

THE RESEARCH WORKER'S REQUIREMENTS

In both academic and industrial research day to day copying requirements arise for facsimiles of documents in various numbers There is always, of course, the initial problem of transforming the manuscript of a new piece of work into a neat layout for reproduction on a comparatively large scale for the purpose of publication It is not proposed to go into this matter which is largely a question of publishing economics It is when the document already exists in a presentable layout, and further copies in small numbers are required immediately to enable the fullest possible use to be made of the information therein, that one looks around and asks 'Where in this atomic age is the automatic machine which will do this for me while I wait?' Conferences, committees and panel meetings even in the best regulated organizations sometimes call with varying degrees of urgency for the last minute preparation of further copies of documents for prior consideration and subsequent discussion at those gatherings Experimental work may necessitate having at hand on the bench in the laboratory for purposes of control or step by step observational comparison a copy of a set of data in tabular or graphical form, a wiring diagram, a dissection diagram or a photomicrograph Opposition proceedings or other legal formalities in connection with patents, with which a research worker may be concerned, may require the submission of copies of laboratory notebooks, specifications or other documents within a certain time limit The research worker may embark upon a literature search prior to initiating a new programme of experimental work The labour of making a manual record of the information located generally makes a literature search a tedious task The need to make a translation of a foreign paper may arise and the paper may contain various figures with foreign captions and legends which need to be reproduced in the translation with the captions *etc* in English Publications may be out of print and subject to only small spasmodic demands for further copies by research workers in the field, which do not justify the cost of reprinting on the part of the publishers, or research workers may be faced with the expense of buying bound volumes containing much unwanted material The importance of providing efficient solutions to these problems of document copying was strongly emphasized at the Royal Society Scientific Information Conference held in London in July, 1948[1]

CLASSIFICATION OF COPYING PROCESSES

If copying processes are examined as a group it is found that they can be classified in the following manner

	Materials used
1 Copying processes	
1 1 Manual (composition) copying methods	Carbon paper Hectograph Wax stencils Offset plates
1 11 Manuscript	
1 12 Typescript	
1 13 Typesetting	
1 2 Photocopying methods	
1 21 Contact copying	
1 211 Transmission copying	Blue print
1 212 Reflex copying	
1 2121 Simple reflectography	Diazo Silver halide
1 2122 Screen reflectography	Diazo
1 22 Projection copying	Plates, film, microfilms, paper, xerographic plates
1 23 Scanning methods	Materials for phototelegraphy 'Forograph' stencils

Various combinations of processes and materials other than those shown in this scheme may be used in practice, but the general relationships are evident We are not concerned here with methods under *1 1*, which are necessarily comparatively slow and error prone Under *1 2*, methods *1 21* and *1 22* offer at present the most economical and convenient ways available to satisfy the requirements outlined above Scanning processes *1 23*, although of great value in other fields such as phototelegraphy for newspaper work and for large government departments, have not been developed for the small scale user It is interesting to note, however, that as a result of recent tests in the U S A a service there for the high speed transmission of documents may soon be based on these processes

Of the contact copying methods *1 21*, the transmission copying processes *1 211 e g* blue printing by the ferroprussiate process, ferrogallic printing and dye line printing are restricted in scope to the production of copies through transparent or translucent one sided originals, although of course they find very wide application in the copying of engineering drawings

Most of the equipment now available for copying work on the small scale is based on reflex copying methods[2] *1 212* Typical machines include the 'Copycat', 'Rectophot' and 'Ruthurstat' which fall within class *1 2121* and make use of silver halide materials These materials have the disadvantages that they require five processing stages subsequent to exposure *viz* developing, washing, fixing, washing and drying, which must be repeated to give a positive copy from the negative so obtained, and must be carried out in subdued light

In recent years a process *1 2122* has been developed in Holland which, by using a fine screen, has enabled diazo materials to be used in reflex copying This is the 'Retocee' process[4-6] and it possesses the advantages that it produces a positive copy directly in a few minutes, consists only of the two steps exposure and development, can be used in a normally lighted room and will reproduce full-tone and half-tone photographs satisfactorily New machines based on this process were demonstrated at the Exhibition arranged for the Royal Society Scientific Information Conference An older model has been in successful operation in the author's department in I C I for over a year

Projection copying methods[7] *1 2a* have so far been available only for use with silver halide materials, with the consequent disadvantages mentioned above as far as the occasional but rapid production of a few copies is concerned For large scale copying establishments, however, where copying work is carried out on a continuous production line basis, these disadvantages may be nullified Microfilm copies, which come within this class, are valuable from the point of view of ease of storage and transmissibility although, on the other hand, many research workers regard them as inconvenient to handle and to read The 'Photostat' apparatus is also a well known example in this class, it produces copies directly on to silver halide paper and processing is carried out in the machine itself except for the washing and drying Two developments in the U S A which have recently been described also fall in class *1 2a* The first is the Land process[8] which carries out the entire production of a positive photograph within a specially designed camera The second is xerography[9] which uses a special plate upon which an electrostatic image is produced and this can be transferred on a resinous powder to paper and fixed thereon Processing is claimed to be dry and rapid It is too early yet to assess the value of these processes for document copying work

CHOICE OF PROCESS

In assessing the merits of these various processes for day to day use the following questions must be considered What type of load will fall upon the apparatus? How quickly would a copy normally be required? How many copies are needed? How convenient is the process to accommodate and operate in the space available? How easy is it to operate? What quality of result does it give? How versatile is the process as regards the type of original it can handle? What is its capital cost? What are the running costs as regards power, materials *etc*? How easy is the copy to consult? It will be found that these considerations sometimes conflict and it would require a much more comprehensive discourse than this short article to weigh up in detailed answers to these questions the relative merits of the available processes It is hoped however that a general indication of relative suitability has been given above Further data are to be found in the *Royal Society Scientific Information Conference Report*[2] and, on the diazocopying processes in particular, in a recent article by the present writer on 'The Principles and Possibilities of Diazocopying Processes' in the *Journal of Documentation*

FUTURE DEVELOPMENTS

The Royal Society Scientific Information Conference studied the commercially available photographic methods of reproduction and concluded that wider use of such methods would be of benefit to science It therefore recommended that the photostat, rather than the reflex, process should be used in large establishments where machines can be kept fully occupied The reflex process is particularly suitable for a library or laboratory where only occasional copies are required The potential value of screen reflex, dry process, diazo printing should be publicized among scientists and industrialists, and the availability of such machines and materials should be facilitated Economical devices and processes should be developed whereby bibliographical lists can be reproduced in the form of a card index, and card indexes can be reproduced as lists Machines which automatically produce multiple copies of folded index slips and single copies of index cards should be publicized

In response to these recommendations the initiation of a programme of research into non-silver photographic processes for document copying is at present under consideration by the D S I R

A good deal of useful work can be done too in the field of standardization For instance, the standard sizes of sensitized materials (½ plate, ¼ plate *etc*) do not correspond to the standard sizes of index cards, so that the use of photocopying processes to reproduce index cards entails at present a wasteful and time consuming trimming operation It is encouraging to see that the British Standards Institution has already appointed a Committee (PHC/12) to prepare *British Standards* dealing with the photographic aspects of document reproduction This Committee has prepared draft standards for sizes of sensitized materials for the reproduction of textual documents and a survey has been carried out of existing apparatus for photocopying

It should also be noted that the British National Committee on Documentation (the national body representing this country in the International Federation for Documentation) was invited to appoint an advisory committee on documentary reproduction representing all interested bodies (Recommendation 19 2) No active steps are being taken by this committee until the results of the B S I Committee's work are available

The above mentioned bodies would welcome the views of both individuals and associations of research workers regarding the ways in which they consider the different types of machines and materials for photocopying could be made to serve them better

This article has been written at the suggestion of the Information Services Committee of the Royal Society to draw attention to Recommendation 20 of the Royal Society Scientific Information Conference, July 1948

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The Merck Research Laboratories

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AT the dedication of the Merck Research Laboratories in 1933, SIR HENRY H DALE, in outlining the fundamental policies that were to guide the progress of the laboratories, stated 'You who work here will be free to choose your problems according to the needs of the time and the promise of advance offered by current progress in science, you will be able to give intense cultivation to the fertile areas, to raise the crops which are likely to give yield, and to put in the sickle where the harvest stands ripe for gathering.'

These were indeed prophetic words From these constantly expanding Merck laboratories have come, in turn, original and important findings in medicinal chemistry and nutrition, among others the widely recognized pioneering work in the vitamins of the B complex, from the synthesis of vitamin B_1 to the isolation of vitamin B_{12}, the large scale development and production of the antibiotics, penicillin and streptomycin, and the highly critical commercial development of the adrenal cortical hormone, cortisone

HISTORY

The history of Merck & Co, Inc, and its predecessor companies is virtually a review of the development of fine chemical manufacture in the U S A The origin of the companies which are represented in the present day organization through a succession of personal and corporate combinations dates back to 1818, two years prior to the discovery of quinine The establishment of the business under the Merck name, however, took place in 1891, when GEORGE MERCK, son of the then directing head of E Merck, Darmstadt, Germany, came to the United States and organized the firm of Merck & Co, with offices in New York

In the beginning the business was largely devoted to the importation of drugs and chemicals, but a few years later became an independent manufacturing enterprise which subsequently produced an extensive line of drugs and chemicals for the professions and industry Within a few years, Merck was one of the leading American producers of chloral hydrate, iodine preparations, bismuth salts, acetanilide, narcotics, salicylates, alkaloids, disinfectants and other important products, including a comprehensive line of prescription chemicals

During the 1914–18 war the company was reorganized as an independent American enterprise and, in 1927, was consolidated with the well known and highly regarded firm of Powers-Weightman-Rosengarten Company of Philadelphia under the name of Merck & Co, Inc The consolidation brought together two great chemical companies, the founders of which were identified with the very beginnings of modern chemistry and the products of which were widely and favourably known for their high standards of purity throughout the fields of medicine, pharmacy, chemistry and industry.

THE MERCK LABORATORIES

Thoroughly imbued with the high ideals and progressive spirit of the founders of these two successful enterprises, and under the leadership of men raised and trained in the finest traditions of the American chemical industry, Merck & Co, Inc, in 1933, opened new and enlarged laboratories for its research workers The laboratories were dedicated in the belief that research work carried on with patience and persistence will bring new life to industry and commerce and in the faith that in such laboratories science will be advanced, knowledge increased, and human life win greater freedom from suffering and disease Though, today, the present immense organization of scientific workers in the Scientific Areas of the Company has outgrown its original modest beginnings, the fundamental idea of research for the benefit of mankind rather than with the profit motive is still the guiding principle of Merck research

EARLY RESEARCH

The early research of the Merck Laboratories was concerned mainly with anaesthetics alkaloids and choline derivatives Following the prediction of C D LEAKE in 1930 that vinyl ether would combine the potency of ethyl ether with the rapidity of induction characteristic of ethylene, W L RUIGH and R I MAJOR, in 1931, prepared pure vinyl ether[1] Its rapid decomposition on exposure to light and air, its tendency to polymerize and its high volatility all limit the usefulness of the pure compound in anaesthesia but these difficulties were successfully overcome by the development of *Vinethene*, a rapidly acting anaesthetic especially useful in short operative procedures

O LOEWI, in 1921, showed[2] that stimulation of the vagus produced a substance in the perfused heart capable of parasympathetic activity on another heart H DALE later showed[3] that the substance acetylcholine was liberated at the motor endplates of parasympathetic and somatic motor nerves following the passage of a nerve impulse Acetylcholine is rapidly destroyed by blood and tissue esterases in the body and hence its effect is transient The development of the more stable acetyl-β-methylcholine chloride afforded a specific, *mecholyl chloride*, which, as first demonstrated[4] by I STARR in 1933, by its stimulation of the parasympathetics promptly terminates an attack of auricular paroxysmal tachycardia

By introducing a process for the production of *synthetic ephedrine*, the Merck Laboratories made a significant contribution to the independence of American medicine from foreign sources of supply of essential drug material

THE VITAMINS

Since 1934 the name Merck has been identified with American leadership in the synthesis, development and large scale synthetic production of vitamins Following an initial exploration of the possibility of synthesizing vitamin C, the Merck Laboratories began the collaboration with R R WILLIAMS that was to lead to the now familiar but still brilliant synthesis[5] of vitamin B_1 As a result of several years of intensive work, Williams and his co-workers in 1934 were able to devise a method for securing consistent yields of the anti-neuritic vitamin hydrochloride from rice polishings In cooperation with Merck & Co, Inc sufficient of the precious natural vitamin in the pure crystalline state was obtained to facilitate the investigation and ultimate successful synthesis of the pyrimidine moiety and of the vitamin itself The culminating stage of final successful commercial synthesis was soon accomplished and followed the course of the vitamin B_1 synthesis devised by R R WILLIAMS and J K CLINE[6]

The work[7] of P GYORGY showed that the rat pellagra or dermatitis, at one time confused with human pellagra, could be cured by a factor present in yeast to which he gave the name vitamin B_6 In 1938 the vitamin was isolated simultaneously by a number of investigators[8] In the course of a year, the structure of the vitamin was elucidated and the vitamin was synthesized[9] by S A HARRIS and K FOLKERS

In 1933 R J WILLIAMS and his collaborators had discovered[10] an acidic substance of widespread occurrence which stimulates the growth of yeast During subsequent years Williams was able to concentrate this yeast growth factor which he called pantothenic acid and to obtain as a final product a calcium salt which he estimated to have a purity of about 90 per cent Williams and his co-workers showed that pantothenic acid consisted of β-alanine in combination with a hydroxy acid and almost simultaneously Wisconsin and Californian workers came to the conclusion that the chick anti-dermatitis factor and pantothenic acid were one and the same substance

For some time before this, research work on the chick anti-dermatitis factor had been in progress in the Merck Research Laboratory, and in the spring of 1939 the collaboration of R J Williams was obtained and a mutual interchange of unpublished data took place The microbiological assay method dependent on the stimulation of the growth of micro-organisms by pantothenic acid, developed by Williams and his co-workers, was invaluable in the investigations which led to the isolation of the lactone moiety of the vitamin molecule from which, by condensation with β-alanine, synthetic salts of pantothenic acid were finally prepared

The growth factor, biotin, which cures rats and humans of the skin disease known as egg-white injury, identified as vitamin H and as co-enzyme R, was synthesized by S A HARRIS, D E WOLF, R MOZINGO and K FOLKERS in 1943[11] Its structural formula had been previously announced by V DU VIGNEAUD and his co-workers at Cornell University Medical College[12] Known to consist of a 5-membered urea ring fused to a 5-membered cyclic ether having a normal valeric acid side chain further studies, in collaboration with a group of workers from the Merck Laboratories, some of them previously experienced in the isolation and structural determination studies of vitamins B_1, B_6 and pantothenic acid, confirmed by desulphurizing reductive cleavage that the fundamental ring structure was a thiophene and that biotin is 2'-keto-3,4-imidazolido-2-tetrahydrothiophene valeric acid

Although it has recently been shown that folic acid, a new member of the vitamin B complex, and to some extent thymine, a basic cell constituent of the body, are both effective in producing blood regeneration in pernicious anaemia and some other macrocytic anaemias, they do not prevent, control or relieve the symptoms arising from degeneration of the spinal cord Moreover, it has been recognized that many concentrates of liver, with high potency in the treatment of pernicious anaemia, contain only infinitesimal amounts of folic acid Accordingly, the search for the potent anti-anaemic factor continued The search was notably hindered by the lack of any reliable assay method to guide the labour of fractionation The difficulties were lightened when, in 1947, M S SHORB reported[13] finding in liver extracts a growth factor (LLD) required by *Lactobacillus lactis*, Dorner, in concentrations bearing an almost linear relationship to the unit potency of the extracts used in the treatment of pernicious anaemia Guided by this assay, E L RICKES, N G BRINK, F R KONIUSZY, T R WOOD and K FOLKERS were able to purify further clinically active liver fractions, and to isolate[14], in minute amounts, a red crystalline compound vitamin B_{12}, highly active for the growth of *L lactis* and with a potency of 11,000,000 LLD unit/mg In the clinical treatment of pernicious anaemia in relapse, intramuscular doses of as little as one microgram have given strongly positive haemopoietic response with prompt increase in the circulating reticulocytes, red cells, and haemoglobin

The most notable achievement of the Merck Laboratories in the field of fat-soluble vitamins was probably the contribution[15] of E FERNHOLZ and J FINKELSTEIN to the chemistry of vitamin E Although the existence of the so-called anti-sterility vitamin was first brought to light in 1922, the isolation and chemical investigation of vitamin E was hindered, partly because of the rather troublesome test method, and partly by the difficulty of fractionating the complex mixture present in the unsaponifiable fraction of wheatgerm oil In 1936, H M EVANS, O H EMERSON and G A EMERSON were able to isolate as crystalline allophanates, the alcohols α- and β-tocopherol[16] The first major advance in the chemistry of α-tocopherol was made by Fernholz who found that pyrolysis at 350°C yielded duroquinol and later, by a brilliant piece of degradative work arrived at the conclusion that α-tocopherol was a chroman derivative Synthesis by the condensation of pseudo-cumoquinol with phytyl bromide (phytol, phytadiene) and resolution of the racemic synthetic product through the bromo camphorsulphonate showed the correctness of Fernholz' conclusions

THE SULPHONAMIDES

The introduction of the sulphonamides constituted one of the greatest advances of all time in the chemical treatment of disease One of the pioneer manufacturers of sulphanilamide, Merck also was the first to produce sulphapyridine in the United States after its development in England, and later became one of the leading large scale producers of sulphathiazole and other sulpha- drugs Among the newer drugs of this series introduced by Merck is *Sulphaquinoxaline* which has demonstrated efficacy in the treatment of cecal coccidiosis in chickens and is consequently of great economic importance

THE ANTIBIOTICS

With the constant urge and necessity for exploration of new avenues of approach to the problem of microbial antagonism, it is not surprising that enormous interest was aroused in industrial research laboratories by the paper, *The Bactericidal Effect of an Extract of a Soil Bacillus on Gram-positive Cocci*, published[17] in 1939 by R J DUBOS, one-time student of soil biology under S A WAKSMAN at Rutgers University Before the end of that year, in connection with Dubos, investigators in the Merck Laboratories started work on the antibiotic *Tyrothricin*, a mixture of polypeptides derived from an aerobic sporogenous bacillus, *B brevis*, work that was to develop into the commercial production of tyrocidine and gramicidin, now used as local antiseptics for a variety of purposes Consequently, following the arrival of Florey and Heatley in the United States in 1941, Merck was able to play a pioneer role in the wartime commercial production of penicillin During 1944 a plant for the production of penicillin was erected by Merck and Co, Ltd, in Montreal and put into commercial operation within six weeks from the actual start of construction

The fundamental research work behind the enormous commercial undertaking has only recently been published in the monumental monograph *The Chemistry of Penicillin* in which the labours of British and American scientists on the problems of the structure and synthesis are recounted in detail[18] The work of Folkers, Peck, Kaczka, Mozingo, Scudi, Woodruff and Trenner on the structure of benzylpenicillin, desthiobenzylpenicillin, penilloic and penicilloic acids, on physical methods of analysis, and on microbiological assay methods is presented in full

Following the isolation of streptomycin from *Streptomyces griseus* by S A WAKSMAN[19] and his students in 1944, the chemical, pharmacological and clinical investigations by Merck scientists and their collaborators enabled the company to go into large scale production of this valuable antibiotic, with world-wide acceptance as a valuable adjunct to established methods of treatment in arresting certain types of human tuberculosis The knowledge and experience gained by the intensive labour of developing the antibiotics from experimental small beginnings to large scale commercial production is reflected in the drop in price of streptomycin, originally £5 a gram to its present U S price of less than 4*s* a gram To keep pace with modern trends much experimental work is now in progress in the investigation of still more effectively and specifically potent antibiotics

CORTISONE

The most recent large scale project of the Merck research organization and one that shows to best advantage the close cooperation between the various divisions of the Merck organization, the Scientific Areas and the collaborating academic and institutional workers, is concerned with the synthesis and large scale production of the adrenal cortical hormone, E C KENDALL's compound E, cortisone

Wartime interest in the adrenal cortical hormones led to a cooperative research arrangement between KENDALL and the Merck Laboratories Dr J VAN DE KAMP and his associates undertook large laboratory scale production of intermediate products which KENDALL hoped would lead to a synthesis of compound A This assistance proved to be of great help and culminated in 1944 when Kendall was able to announce[20] his successful synthesis of compound A Unfortunately, compound A was found to have little physiological activity in the treatment of shock, fatigue and related conditions Interest shifted accordingly to compound E Finally, L H SARETT successfully completed the first synthesis of cortisone from desoxycholic acid [1] Further cooperative work with E C KENDALL led to a simpler production method for cortisone

The development of this laboratory synthesis into a practical commercial method of production was of necessity laborious Under the leadership of M TISHLER and J VAN DE KAMP, a group of development chemists of the Merck Laboratories devised less tedious and more productive procedures and so provided sufficient material[8] for those preliminary clinical evaluations which led to the dramatic demonstrations[22] of its value in rheumatoid arthritis by P S HENCH and his associates at the Mayo Clinic

Those first cases of rheumatoid arthritis and rheumatic fever treated with cortisone not only opened the door to possible control of these widespread disabling diseases but provided a new concept of the cause and nature of such diseases, and in so doing made it imperative that no effort could be spared to make this vital compound readily available in commercial quantities

Aided by engineering research and design, the development procedures worked out by van de Kamp and his co-workers gradually passed through pilot plant levels into limited factory production so that material is available for an extensive clinical research programme now being carried out by outstanding experts in the U S A and at widely scattered centres throughout the world Today, cortisone has already been tried in over fifty different diseases Current research in the cortisone field is being vigorously pursued to improve present processes to discover more available intermediates and to examine the possibility of total syntheses

This constantly expanding research on the adrenal cortical hormones differs in no way from that in other fields In all such developments of a new drug from the fundamental research of the discoverers and their scientific consultants to the final marketing and distribution of the remedy to the physicians for the treatment of their patients, the collaboration of the various members of a well developed and closely integrated organization is highly essential The preliminary pharmacological investigations of The Merck Institute for Therapeutic Research and its associated academic collaborators guide the development of the drug until the remedy is suitable for clinical investigation The large scale manufacturing operations which follow as the result of engineering research and design and factory research in production problems are carefully controlled to assure compliance with and adherence to company and federal standards Finally, the problems of production, packaging, shipping, marketing and distribution must receive adequate consideration before the new drug can become generally available to the average patient

The provision of the new drugs so necessary for the development of medical science is regarded as the most important single medical problem of today Only by the constant labours of the highly organized industrial laboratories and their collaborating fellow scientists can this need be satisfied to a high degree

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Miscellaneous Notes

AGRICULTURAL RESEARCH COUNCIL

Changes are being made in the administration of the Foot-and-Mouth Disease Research Station. The work at this Station has up to the present been conducted under the scientific direction of a Committee appointed by the Minister of Agriculture with the financial and administrative arrangements being made by the Ministry The Station is now to join the family of research institutes, being financed by grant-aid from the Ministry of Agriculture and coming under the scientific oversight of the Agricultural Research Council The new Governing Body is being constituted by the Minister of Agriculture and the Secretary of State for Scotland, in agreement with the Agricultural and Medical Research Councils as a Company limited by guarantee and without share capital, and in the membership of the Governing Body representation of scientific interests both in medicine and animal health has been secured Membership of the Governing Body is as follows Dr A N Drury CBE, MD, FRS, (Chairman), Dr C H Andrewes, MD, FRS, Professor S P Bedson, MD, DSc, FRCP, FRS, T Dalling, MA, MRCVS, FRSE, Professor R E Glover, MA, BSc, FRCVS, Dr J Russell Greig, CBE, PhD, MRCVS, FRSE, Professor Wilson Smith, MD, FRS and Professor W I B Beveridge, MA, DVSc (Sydney)

ROYAL SOCIETY OF ARTS

As part of the Society's celebrations of the centenary of the Great Exhibition of 1851, which it originated, and as a constructive effort to assist the nation in its present difficulties, the Council of the Royal Society of Arts propose to award on 1 May 1951 a Prize of a Gold Medal and a sum of £500 for a means of promoting the production or the economic utilization of food in Britain'

The proposal may be quite general or may be concerned with any particular branch or aspect of food production Proposals submitted must be as well documented as possible and the Council have therefore decided not to prescribe any fixed limit of length for written communications At the same time they wish to impress upon all competitors the importance of conciseness in their remarks The judges may require some practical demonstration of any mechanical device or process submitted

Entries must reach the Secretary of the Roya Society of Arts, John Adam Street, Adelphi, London, W C 2, by 1 March 1951

INSTITUTE OF PHYSICS

At the Annual General Meeting of the Institute of Physics, Professor W E Curtis (Professor of Physics, King's College, University of Durham, Newcastle-upon-Tyne) was elected President

Professor F G Cox was elected a Vice-President, and Dr F P **Bowden** and G R **Noakes** were elected Ordinary Members of the Board The Honorary Treasurer, E R **Davies**, and the Honorary Secretary, Dr B P **Dudding**, were re-elected Professor H W **Thompson** joins the Board as the new representative of the Faraday Society

COMING EVENTS

Annual Exhibition and Symposium of Scientific Instrument Manufacturers' Association, Examination Hall, Queen Square, London, 5–8 September

Sixth National Chemical Exposition, Chicago, 5–9 September

Royal Netherlands Industries Fair, Utrecht, 5–14 September

Seventeenth National Radio Exhibition, Castle Bromwich, Birmingham, 6–16 September

International Nuclear Physics Conference, Harwell and Oxford 7–13 September

Second Biennial Congress of International Union of Leather Chemists' Societies, Regent St Polytechnic, London, 10–13 September

International Meeting of Associations for Advancement of Science, U N E S C O, Paris, 11–12 September

Annual Meeting of French Association for Advancement of Science, Toulouse, 11–16 September

Sixth Educational Graphic Arts Exhibition, Chicago, 11–23 September

Eighth Annual Meeting of Electron Microscope Society of America, Hotel Statler, Detroit, Michigan, 14–16 September

International Congress on Electron Microscopy, Paris, 14–22 September

23rd Congress of Industrial Chemistry, Milan, 17–23 September

International Conference on Spectroscopy at Radio-Frequencies, Netherlands Physical Society, Amsterdam, 18–23 September

Royal Agricultural Society of Kenya Annual Show, Nakuru, 19–21 September

Spectroscopy and Molecular Structure and Optical Methods in Investigation of Cell Structure, Cambridge, 25–28 September

International Railway Congress Association Meeting, Rome, 25 September–4 October

Fourth National Congress of Associazione Italiana di Metallurgia, Florence, 28 September–1 October

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New Books

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London E and F N Spon Ltd 1949 63s net

THOSE who have had occasion to search the literature for specific facts on chemical processes based on petroleum raw materials will gratefully welcome the appearance of this compilation of hitherto widely scattered data The author has dug deep, but selectively, and sifted his matter with care

The book deals with the subject primarily from the point of view of the mechanism and thermodynamics of the processes involved, the effect of reaction conditions, and the ultimate application of the processes to commercial production Starting with a general outline of petroleum processing, he discusses the synthesis and reactions of carbon monoxide-hydrogen mixtures and the manufacture or separation of the different hydrocarbon raw materials The production and reactions of specific types of chemicals—ketones, alcohols, acids, olefin oxides *etc* are then covered, finishing with a brief chapter on chemical by-products from petroleum refining

Useful appendices are included giving charts showing the routes to petroleum chemicals and statistics on production and consumption of petroleum and chemical by-products (With regard to the last mentioned, it is understood that the fact that these are rather out of date is a fault of the times in which we live rather than of the author)

With the rapidly growing importance and economic significance of the production of chemicals in this country, this book will serve as an authoritative guide both for the industry itself and for users of the products Further, it will be found of considerable value to lecturers, covering as it does many branches of chemistry not adequately covered in general chemical treatises and emphasizing the contribution of the petroleum industry to scientific knowledge in fields such as the reactions of the hitherto intractable paraffins, the substitutive chlorination of olefins, the alkylation process, the development of highly specific catalysts, and a better knowledge of their functioning

The book is well bound and printed, adequately indexed, and the author's clear and concise style makes for easy reading In spite of its high price, it should be found on the desks of all interested in the petroleum chemicals industry

C L **Gilbert**

A Monograph of Clavaria and Allied Genera

E J H CORNER

Annals of Botany Memoirs, No 1
(*xiv + 740 pp, 298 illus, 15 plates, 9½ in by 6¼ in*)
London Oxford University Press 1950 105s net

WE seem to be witnessing at the moment a welcome blossoming of botanical literature in Britain and it is indeed pleasing that the Annals of Botany Company should assist in this blooming by sponsoring a new series of which this monograph is the first. It sets a high standard for its successors, for CORNER's book on clavarioid fungi is an imposing monograph bringing together existing systematic knowledge and adding much that is new from his extensive work on these fungi both in England and in S E Asia.

The author deliberately avoids the use of the family name Clavariaceae to embrace these fungi because he feels that they by no means form a natural group. This century is seeing the breakdown of the Friesian classification of higher Basidiomycetes. The work of HEIM and others of the French school has shown that both Agaricaceae and Polyporaceae are unnatural assemblages, and now Clavariaceae must be added to the list.

The work under review is essentially a systematic treatment of the genera *Aphelaria*, *Araeocoryne*, *Caripia*, *Ceratellopsis*, *Chaetotyphula*, *Clavaria*, *Clavariachaete*, *Clavariadelphus*, *Clavicorona*, *Clavulina*, *Clavulinopsis*, *Deflexula*, *Dimorphocystis*, *Hormomitaria*, *Lachnocladium*, *Lentaria*, *Mucronella*, *Myxomycidium*, *Physalacria*, *Pistillaria*, *Pistillina*, *Pterula*, *Pterulicium*, *Ramaria*, *Ramariopsis*, *Scytinopogon* and *Typhula*. It is intended for laboratory and field use.

One of Corner's chief contributions to Mycology is his study of developmental anatomy of the larger fungi and his analysis of how different hyphal systems cooperate in the production of the final result. The present work contains a great deal of most interesting information about the anatomy of clavarioid fungi illustrated by some of the most beautiful illustrations of basidiomycete structure that have ever been published. Especially intriguing are those species *e g Ramaria cyanocephala*, in which the hymenium gradually thickens with age leaving exhausted basidia and some detached spores immersed in the older and deeper tissues. However, the present volume is only the first part and is supposed to be introductory to a further work on the morphology of clavarioid fungi. Those who have turned over the pages of the systematic volume will look forward eagerly to the promised one on morphology.

Besides the black and white pictures there are fifteen coloured plates very beautifully executed and produced, but it is most regrettable that part of the cost of these, as pointed out by Professor FRITSCH in his foreword, should fall on the author.

Corner was working in Malaya when it was invaded and he fell into Japanese hands. In a world torn by hatred it is heartening to find that he acknowledges indebtedness to those who were technically his enemies, but who had the generosity and breadth of mind to enable him to continue his work under their protection.

There can be no doubt of the importance of this contribution to the morphology, taxonomy and phylogeny of clavarioid fungi, but it is essentially a work for libraries and museums rather than for individuals, and its price is necessarily high. The author would render a great service to students of Mycology in the universities if he would produce a short work on the Morphology and Developmental Anatomy of the Higher Fungi richly illustrated by his beautiful drawings.

C T INGOLD

Gmelins Handbuch der anorganischen Chemie

Eighth edition Edited by E H E PIETSCH
Aluminium (A 8) Ternary Alloys
Aluminium-Iron-Carbon, Aluminium-Iron-Silicon
(*ii + 1235–1370 pp, illus 404–481, 10 in by 7 in*)
Weinheim/Bergstrasse Verlag Chemie G m b H, 1950

THIS volume deals with two important groups of aluminium alloys, for which it gives many excellent phase diagrams, a review of physical and mechanical properties and information on corrosion and chemical analysis. It has been compiled with that care and attention to detail which have gained for Gmelin international recognition as a reference work. This particular part will be of special interest to metallurgists. Its appearance is welcome evidence that the difficulties of the post-war period have now been largely overcome, and that the production of the remaining volumes, a considerable number of which are still missing, is likely to go on at an increasing rate.

H J EMELÉUS

Books to Come

Science of Petroleum, Vol V, Part I Crude Oils, their Chemical and Physical Properties *Edited by* B T BROOKS and A E DUNSTAN (*200 pp, illus, 11 in by 8 in*) London Oxford University Press 42s net

Mathematical Solution of Engineering Problems J JENNINGS (*210 pp, 80 illus, medium 8vo*) London E and F N Spon Ltd 25s net

RESEARCH SUPPLEMENT

Characterization of d-Glucosamine

P W KENT, B Sc, Ph D, F R I C

d-Glucosamine has been converted into crystalline aldehydo derivatives and a furanose glycoside of the sugar has been obtained The preparation and chromatographic behaviour of N-*(2,4-dinitrophenyl) substituted glucosamine and related compounds is described as a method of detection and separation of the amino sugar in the presence of uronic acids and neutral sugars*

THE amino sugars are of considerable importance as components of biologically important compounds notably some tissue components, bacterial polysaccharides, blood group substances, heparin *etc* In the majority of substances studied the amino sugar is firmly bound and few methods[1] are available for the study and isolation of these sugars

In ovomucoid[2], hyaluronic acid[3] and the lipoid bound polysaccharide *Mycobacterium tuberculosis*[4], *d*-glucosamine is found in the pyranose form The growing significance of amino sugars makes it imperative that as many reference compounds as possible should be synthesized Accordingly, a number of crystalline derivatives has now been made in order to facilitate the characterization of the various forms of glucosamine, *Figure 1*

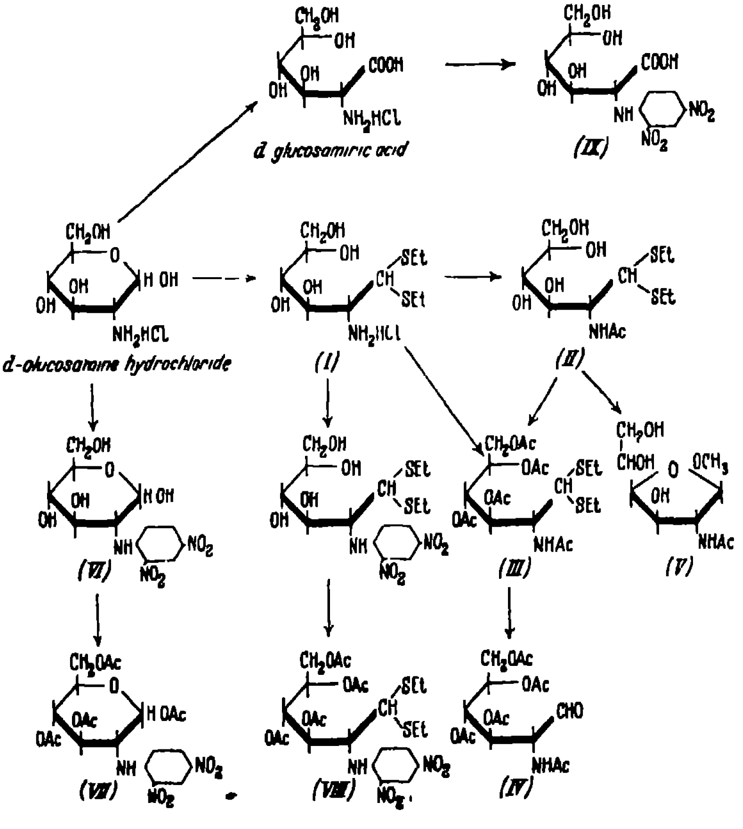

Figure 1 Various forms of glucosamine

d-Glucosamine hydrochloride was reacted at room temperature with ethyl mercaptan in the presence of excess concentrated hydrochloric acid (density 1 4) Removal of the acid by means of lead carbonate and evaporation of the solvent gave a product which crystallized readily as *d*-glucosamine diethyl mercaptal hydrochloride *I* m pt 75 to 76°C angle of rotation $[\alpha]_D^{21}$ − 18 0°(H_2O, *c* 0 16), found C 37 0, H 7 38, N 4 11, S 19 6 per cent $C_{10}H_{24}O_4NS_2Cl$ requires C 37 2, H 7 45, N 4 35, S 19 9 per cent Acetylation of *I* with acetic anhydride in methanol yielded N acetyl *d*-glucosamine diethyl mercaptal *II* m pt 121 to 122°C $[\alpha]_D^{18}$ − 24°(H_2O, *c* 0 4), found C 44 0, H 7 63, N 4 16, S 19 2 per cent $C_{12}H_{25}O_5NS_2$ requires C 44 1, H 7 66, N 4 27, S 19 6 per cent, while further acetylation of *II* (or *I*) with acetic anhydride in pyridine furnished pentacetyl *d*-glucosamine diethyl mercaptal *III* m pt 160 to 161°C $[\alpha]_D^{18}$ + 2°($CHCl_3$, *c* 1 0), found C 48 83, H 7 02, N 2 32, S 12 76 per cent $C_{20}H_{33}O_9NS_2$ requires C 48 49, H 6 6, N 2 83, S 12 95 per cent Pentacetyl aldehydo-*d*-glucosamine *IV* was formed when *III* was treated with a solution of mercuric chloride in acetone[5] This compound *IV* was separated from the reaction mixture chromatographically on a powdered cellulose column and was crystallized from di-*iso*propyl ether, m pt 156 to 157°C $[a]_D^{22}$ + 36° ($CHCl_3$, *c* 0 1), found C 49 1, H 5 75, N 3 33 per cent $C_{16}H_{23}NO_{10}$ requires C 49 4, H 5 91, N 3 59 per cent The aldehydo pentacetate *IV* was strongly reducing toward Fehling's solution, had an absorption band in the ultraviolet region of the spectrum at 2,650 Å and restored the colour to Schiff's reagent in the same way as pentacetyl aldehydo glucose and pentacetyl aldehydo galactose, examined under the same conditions

Treatment of N acetyl-*d*-glucosamine diethyl mercaptal *II* with mercuric chloride in methanol[6] yielded a compound having properties consistent with 2-deoxy 2-acetylamino methyl glucofuranoside *V* $[a]_D^{22}$ − 25° (H_2O, *c* 0 8), found OMe 13 0 per cent $C_9H_{17}O_6N$ requires OMe 13 19 per cent

The furanoside *V* was readily oxidized by periodate ion, utilizing one mol and liberating formaldehyde The compound *V* was hydrolysed by 0 01 N acid at 100°C in three hours ($[a]_D$ − 25° → + 39°) yielding N acetyl-*d*-glucosamine

A new series of crystalline derivatives has been obtained by virtue of the fact that 2,4-dinitrofluorobenzene reacted with *d*-glucosamine (1 mol) under very mild conditions[7] The reactants were shaken for 2 hr in 50 per cent aqueous ethanolic solution in the presence of sodium bicarbonate (2 mol) Evaporation of the solvent yielded N-(2,4-dinitrophenyl)-*d*-glucosamine *VI* m pt 167 to 169°C $[a]_D^{22}$ + 50 0° in ethanol, R_F 0 75, found C 41 6, H 4 20, N 11 9 per cent $C_{12}H_{15}O_9N_3$ requires C 41 80, H 4 35, N 12 18 per cent Acetylation of this compound *VI* with acetic anhydride and pyridine gives a highly crystalline material, tetracetyl DNP glucosamine *VII* [where DNP represents N-(2,4-dinitrophenyl)-] m pt 159 to 160°C $[a]_D^{20}$ + 73°, R_F 0 93, found C 46 56, H 4 34, N 8 03 per cent $C_{20}H_{23}N_3O_{13}$ requires C 46 70, H 4 49, N 8 20 per cent Similarly, tetracetyl DNP glucosamine diethyl mercaptal *VIII* m pt 87 to 88°C $[a]_D^{22}$ − 108 5° in chloroform, R_F 0 96, found C 46 3, H 5 28, N 7 21, S 10 05 per cent $C_{24}H_{33}N_3S_2O_{11}$ requires C 46 52, H 5 35, N 6 79, S 10 35 per cent, and DNP glucosaminic acid *IX* m pt 107 to 108°C, R_F 0 60, found N 11 41 per cent $C_{12}H_{15}N_3O_{10}$ requires N 11 65 per cent were obtained

These substances could be separated readily from uronic acids and neutral sugars by paper chromatography using *Whatman No 1* filter paper and N-butanol (40 per cent) — ethanol (10 per cent) — water (50 per cent) mixture as the eluting agent

The appropriate R_F values (where R_F denotes the ratio of the distance moved by the substance to that moved by the solvent) are indicated above Similarly, good separation could be achieved between DNP glucosamine derivatives and DNP amino acids The reaction between glucosamine and the fluoro reagent was quantitative and there is no evidence to suggest any reaction with neutral sugars Mixtures of neutral sugars, uronic acids and glucosamine could be treated *in situ* with 2,4-dinitrofluorobenzene under the prescribed conditions When two drops of the resulting reaction mixture were applied to the paper chromatogram, the movement of the bright yellow DNP glucosamine could be observed directly Any unchanged dinitrofluorobenzene moved with the solvent front and the neutral sugars could be observed by drying the paper and spraying with aniline hydrogen phthalate solution

By this method the presence of glucosamine has been demonstrated in hydrolysed blood group A substance, heparin and ovomucoid The procedure is being developed to deal with problems in the structural study of mucopolysaccharides and mucoproteins, ribo- and deoxyribonucleic acids

This work has been made possible by a grant from I C I Ltd for which the author expresses his thanks He is also grateful to A W D Huggell for the technical assistance rendered

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Research Correspondence

Heat Transfer by Spray Cooling

It is a remarkable fact that there seems to be no published work on the measurement of the heat transfer to a spray from a hot surface on which it impinges. This note is intended to show how this data may be obtained.

There are two reasons for the importance of determining a relationship between spray cooling heat transfer and the other variables of the system. First, spray cooling is already widely used, and until such a relationship is available the design of a spray cooling system must be empirical and probably inefficient. Secondly, there may be occasions when it is necessary to choose between cooling a hot surface by means of water flowing tangentially over it or by using a system of water sprays; at the moment this can only be done by trial. It was in the course of such a trial that the following results were obtained. If the absent relationship were determined, such a comparison could be made more easily by calculation.

The variables are those of the cooled surface, the coolant (assumed to be water), and the geometry of the jet arrangement. The present experiments have shown that, in general, the effect of each jet may be considered separately as acting alone over the area adjacent to the point of impact on the hot surface. This fact simplifies the problem, since the pattern of a bank of jets is then comparatively unimportant. The variables may be correlated by a dimensionless equation of all likely variables, finding by experiment the importance of each. This equation was assumed to be of the form

$$N_u = A\,(R_e)^l\,(P_r)^m\,(d/D)^n$$

where A, l, m, n are constants to be determined by experiment, and N_u, R_e and P_r are dimensionless factors known as the Nusselt, Reynolds and Prandtl numbers[1]. The ratio d/D is that of the jet diameter to the diameter of the effective area of hot surface that it cools.

If it is assumed that the cooling water hardly alters in temperature, the Prandtl factor may be omitted from the equation. However this is only possible when the surface is cooled to below the boiling point of water. Above 100°C the constants in the equation will be quite different owing to the formation of a steam layer[2].

The following method of heat transfer determination is suitable for both ranges of heat transfer. The heat transfer over the small area of one face of a one inch 'probe', the opposite face being heated by a bunsen or oxyacetylene flame, is derived from the temperature gradient along it. This gradient is found from two or more thermocouples welded on to the copper probe. It gives the temperature of the surface by extrapolation, and the heat flux through it, and the ratio of these factors gives the surface conductivity, i.e. heat transfer coefficient. This has been found to be independent of the surface temperature (below 100°C), so that a relationship like Ohm's law is applicable to the surface boundary layer.

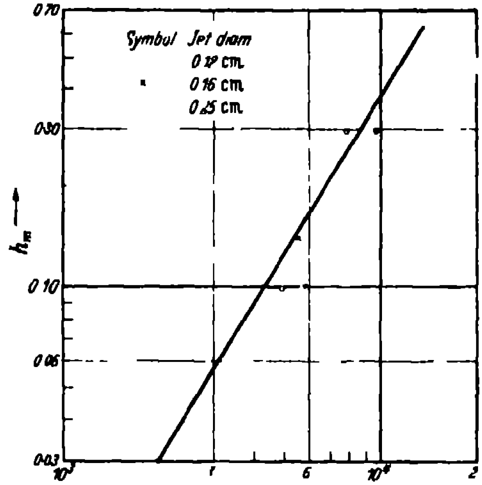

Figure 1. Curve showing empirical relationship $h_m \propto R_e^{4/3}$ for different jet diameters where h_m is the average heat transfer coefficient [cal cm^{-2} (°C)$^{-1}$ sec^{-1}] and R_e is the Reynolds number

By moving the jet over the copper plate, part of the surface of which is the end of the 'probe' [¼ in (6·3 mm) diam], one can measure the heat conductivity over the whole of the region cooled by the jet. To obtain average values of heat transfer, suitable integration then allows determination of the constants in the suggested formula.

The few results in *Figure 1* show the change in average heat transfer over the area of the probe as the Reynolds number, i.e. diameter and velocity, of the jet is altered. In this special case the jet impinges directly on the end of the probe. Although only approximate, these results suggest that l in the equation has a value of about 4/3.

It is intended to make a few measurements on a water cooled hot surface above 100°C, but the problem must be of such general interest that it is to be hoped that some reader will be able to make an extensive and definitive determination of the spray cooling heat transfer.

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(*Received August 1950*)

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Perfluoro Amines

THE fluorination of organic compounds containing nitrogen by means of fluorine on the surface of a 'catalyst', or by cobalt trifluoride, was described recently[1]. Cobalt trifluoride has now been used to fluorinate a series of tertiary amines and the corresponding perfluoro tertiary amines have been isolated in small yield. The properties of these compounds are shown in *Table I*.

Table I

Compound	B pt °C	n_D^{25}	D_4^{25}
$(CF_3)_3N$	−6 *to* −7		
$(CF_3)_2(C_2F_5)N$	20 *to* 22		
$(CF_3)(C_2F_5)_2N$	45·5 *to* 46·5	—	—
$(C_2F_5)_3N$	70·3	1·262	1·736
$(C_3F_7)_3N$	129·9	1·279	1·822
$(C_3F_7)_2(isoC_4F_9)N$	146 *to* 148	1·283	1·811
$(C_4F_9)_3N$	179·3	1·291	1·873

The yield of perfluoro trimethylamine was very low since the fluorination of trimethylamine gave mainly perfluoro dimethylamine and perfluoro methylamine[4]. Of the amines studied, triethylamine, tripropylamine, and tributylamine were available in quantity and the properties of the corresponding perfluoro compounds were determined in more detail than was possible with the limited amounts of the C_4, C_5 and C_{10} amines available.

The boiling points of the perfluoro amines vary regularly with the number of carbon atoms, and the boiling points of perfluoro methylamine (−75° C) and perfluoro dimethylamine (−37° C) lie on an extension of this curve. The boiling points of perfluoro piperidine (49 to 50° C), perfluorocyclohexylamine (75 to 76° C), and perfluoro dimethylcyclohexylamine (116 to 120° C) lie slightly above the curve, and diverge more as the series is ascended. Furthermore, if for the fluorocarbons C_nF_{2n+2} shown in *Table II*[2] the values of boiling point are plotted against (n − 1) on the same graph, then it is found that the curve so obtained lies close to that for the perfluoro amines. The lines diverge as the series is ascended.

Thus it is apparent that the replacement of carbon by nitrogen in a fluorocarbon does not alter the boiling point appreciably even though the resultant compound may contain a smaller number of fluorine atoms (for example *cf* $(CF_3)(C_2F_5)_2N$, C_5NF_{13}, b pt 45·5 to 46·5° C, perfluoropiperidine, C_5NF_{11}, b pt 49 to 50° C, C_6F_{14}, b pt 58° C, and perfluoro*cyclo*hexane, C_6F_{12}, b pt 51° C and perfluoro triethylamine, C_6NF_{15}, b pt 70·3° C, perfluoro*cyclo*hexylamine, C_6NF_{13}, b pt 75 to 76° C, perfluoroheptane, C_7F_{16}, b pt 82° C, and perfluoromethyl*cyclo*hexane, C_7F_{14}, b pt 76° C).

The higher perfluoro tertiary amines are liquids whereas the fluorocarbons above C_9 are solids[2]. Comparison of the refractive index and density of the fluorocarbons with those of the nitrogen-containing compounds with the same number of atoms other than fluorine reveals fairly close agreement (*Table III*).

Table III

Fluorocarbons*			Nitrogen compounds		
Compound	n_D^{25}	D_4^{25}	Compound	n_D^{25}	D_4^{25}
C_8F_{18}	1·267	1·711	$(C_2F_5)_3N$	1·262	1·736
$C_{10}F_{22}$	1·270	1·816	$(C_3F_7)_3N$	1·279	1·822
$C_{11}F_{24}$	1·286	1·837	$(C_3F_7)_2(isoC_4F_9)N$	1·283	1·811
C_7F_{14}	1·276	1·784	$C_6F_{11}NF_2$	1·286	1·787

* Values of n_D^{25} and D_4^{25} for $C_{10}F_{22}$ and $C_{11}F_{24}$ are extrapolated.

The molecular refractions of the perfluoro tertiary amines calculated by the Lorentz-Lorenz expression are shown in *Table IV*.

Table IV

Compound	$(C_2F_5)_3N$	$(C_3F_7)_3N$	$(C_3F_7)_2(isoC_4F_9)N$*	$(C_4F_9)_3N$
MR_D	35·28	49·9[illegible]	(55·03)	6[illegible]
AR_F	1·20	1·21	(1·22)	1·23
AR_N	2·02	2·94	(2·10)	2·3[illegible]

* The values for this compound are quoted with reserve since the density was not determined accurately.

In this table, AR_F gives the atomic refraction of fluorine calculated by assuming that the atomic refraction of nitrogen is 2·74, the same as in tertiary amines[3]. If, however, the atomic refraction of fluorine is taken as 1·25, a value obtained for the perfluoro paraffins[2], then the atomic refraction of nitrogen, AR_N, can be calculated as shown. The molecular refractions of perfluoro piperidine and perfluoro *cyclo*hexylamine are 28·45 and 33·31, and if the atomic refraction of fluorine is taken as 1·22, a value deduced for perfluoro cyclic compounds[2], then the atomic refraction of nitrogen is 2·94 in each case. In view of the experimental difficulty of measuring the low refractive indices recorded here, the agreement is satisfactory although more detailed studies may modify the values quoted.

Table II

C_nF_{2n+2}	C_2F_6	C_3F_8	C_4F_{10}	C_5F_{12}	C_6F_{14}	C_7F_{16}	C_8F_{18}	C_9F_{20}	$C_{10}F_{22}$	$C_{11}F_{24}$	$C_{12}F_{26}$
B pt °C	−78	−37	−2·5	29	58	82	103	125	144	161	178

The perfluoro tertiary amines are chemically inert, and as pointed out earlier[1] should not really be termed amines since they are not basic and in their reactivity resemble nitrogen trifluoride

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An Emission Microscope for Photoelectron Autoradiography

[A short preliminary communication with the above title was made at the Edinburgh meeting of the Physical Society on 19 February 1949]

The now well known method of contact autoradiography suffers from the inherent disadvantage that the photographic impression is limited in resolution just because the source of ionizing particles (usually β-particles) is in actual contact with the emulsion and because the range of these particles in the emulsion is not negligible (the mean range of a 100 kev electron is of the order of 50μ, and for higher energies the range increases somewhat more rapidly than the energy) The method is also limited in that the primary photographic image must of necessity be of unit magnification only

Magnified autoradiography is in principle possible when the radioactive source employed emits electrons of a single energy, and many sources are now available which approximate sufficiently closely to this condition Strong ' internal conversion ' lines are not infrequently found with β-emitters, and they constitute, of course, the main spectral component of particle radiation when transformation takes place by electron capture or isomeric transition As early as April 1944, POOL[1] pointed out the likely importance of such sources ' for certain uses in electron microscopes ' More than three years later, MARTON and ABELSON[2] published the first account of a prototype instrument producing magnified autoradiographs in this way Using the 83 kev internal conversion electrons from ^{67}Ga and a linear magnification of 1 6 they obtained photographs showing a best resolution of about 30μ In the intervening period one of us (N F) had also made plans for the development of an instrument of this type and design was commenced in the summer of 1946 This was completed towards the end of that year (H O W R) and construction was started in the A E R E workshops at T R E , Malvern, in the following spring The instrument, complete except for camera housing, was delivered on 30 October 1948

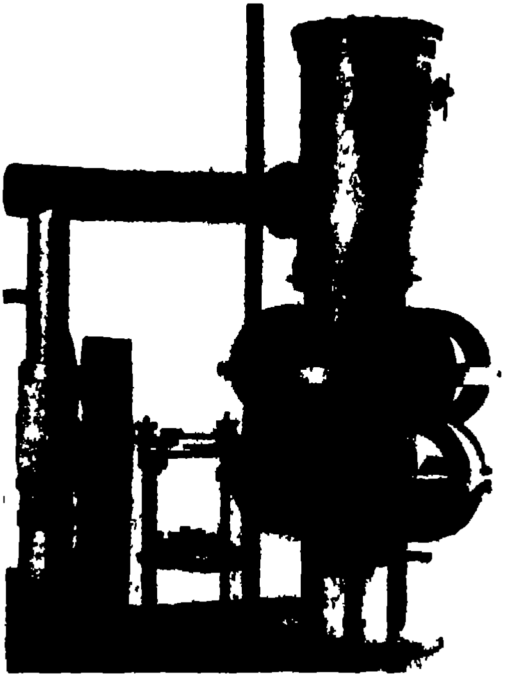

Figure 1 Assembled microscope

Figure 1 shows an external view of the completed microscope The detailed design will be described elsewhere , here it is sufficient to say that the specimen is placed in the lower gap of a two component magnetic lens the field of which is maintained between soft iron pole pieces by the double array of horseshoe-type permanent magnets visible in the photograph Field coils enable changes in the magnetization of these magnets to be conveniently made Adjustment of the shape of the lens field is also available through screw motions by which the axial positions of the soft iron pole pieces can be altered

The performance of the emission microscope has been studied using thorium active deposit as source material[3] This source provides a good test of performance since the electrons used in image formation (ThB *F*-line, 148 kev) comprise only 1/8 of the whole electron radiation of the source. *Figure 2*

Figure 2 Image of brass button

shows the image of a brass button of 0 83 mm diameter formed on a *Kodak NT2a* plate at an electron-optical magnification of 7 using an effective exposure time of 4 5 hr The surface of the button had previously been engraved with a series of intersecting grooves of different widths and depths and the button had then been activated over emanating radiothorium in the usual way The effective aperture of the instrument in this experiment was about 10 ^{4} of the complete sphere Close study of this photograph indicates that a best resolution of about 6μ has been achieved

It is clear that magnified (photoelectron) autoradiography offers possibilities in many directions Biological applications will turn on the successful use of electron-sensitive emulsions and the plotting of images by individual track localization, but in many other fields, for which severe limitation of source strength is not a primary consideration, the simpler techniques of standard electron photography will suffice

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Adhesion of Indium under Static and Dynamic Loading

It is well known that when clean metals are placed in contact they will adhere and an appreciable force is then required to separate them To obtain a sufficient degree of cleanliness it is usually necessary to work under vacuum, using metals which have been degased at a high temperature In air, appreciable adhesion is not usually observed at light loads owing to the presence of intervening surface films of oxide but when sufficient force is applied to cause plastic flow these films may split and metallic junctions form Bowden and Tabor[1] have demonstrated that with such a soft material as indium the adhesive force may equal that of the initial loading

We have been studying the mechanical behaviour of metals during impact by measuring piezoelectrically the force of impact as a function of time A typical experiment consists of allowing a freely suspended hammer weighing about 450 gm and carrying a 0 25 in (0 6 cm) diameter test cylinder to fall towards a similar cylinder supported against the piezoelectric crystal The velocity of approach of the te nde is less than 80 cm sec ^{1}, the axes of are mutually perpendicular so t is circular The appar adhesion, and has been under conditio is comparable with that The experiments were carried the static and dynamic experime to minimize tangential mot

Cylinders of indium w and force/time curves for impac tacting surfaces were made by cutting of metal c 0 02 in (0 5 mm) thick with a shaped as to leave a cylindrical surface 0 25 in in diameter Both specimens were cut within one minute and the impact was made within a minute of cutting the second cylinder *Figure 1* shows a typical force/time curve The force becomes negative at *C* and rises to zero before the end of the contact at *B* This negative force shows that some adhesion has developed between the cylinders during the 2 msec of the impact The maximum force reached in this impact was 11 × 10^{6} dyne, the adhesion was 1 3 × 10^{6} dyne and the area of the dent produced by the impact in the specimen was 8 2 × 10^{-2} cm^{2} For the static experiments, specimens freshly cut as before were pressed together for two minutes Some definite time of loading has to be chosen because indium continues to flow after the application of the load In a static test in which a load of 3 3 × 10^{6} dyne was used, the contacted cylinders subsequently withstood a pull of

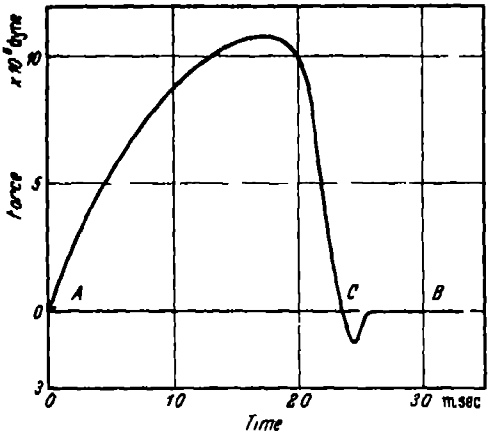


Figure 1 Force, time curve for an impact between cylinders of indium AB shows the time of contact as measured by using the cylinders to switch an electric circuit

3.6×10^{6} dyne and the dented area was $7.0 \times 10^{-}$ cm^2 Although this area is less than the area of the dent produced by the impact described, the adhesion is nearly three times greater

The separated surfaces were examined with a profilometer and microscopically The separated surfaces of the statically loaded cylinders are torn and show that metallic junctions have been broken whereas the surfaces after impact remain smooth *Figure 2* curve **a** is a profilometer trace from the centre of the separated surface of one of the cylinders loaded statically as described and curve **b** is a similar trace from the bottom of a dent produced by the impact Micrographs taken under identical conditions of illumination are shown in *Figure 3* The cutting produces parallel tool marks in the original surface, it will be seen from *Figure 3* **b** that these lines still remain after the impact

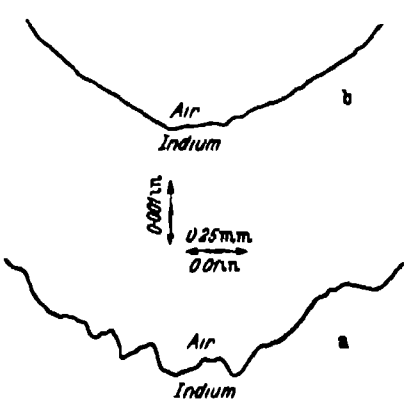
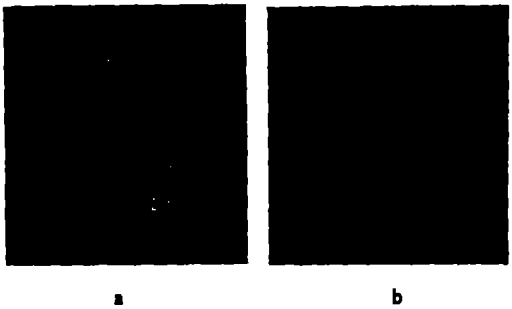


Figure 2 Profilometer traces of dents in indium cylinders, **a** *dent produced statically* **b** *dent produced by impact*



a **b**

Figure 3 Micrographs of the separated surfaces (diameter of field 0.07 cm) **a** *after static loading* **b** *after impact*

The results show that for equal areas of contact the adhesive force and the welded area are less under dynamic than under static conditions SAMPSON, MORGAN, REED and MUSKAT have found that the coefficient of static friction increases with time after a rapidly moving metal slider has been brought to rest on a metal plate and to explain this suggested that the strength of the metallic weld depends on the time of contact The more direct evidence here advanced confirms this suggestion The cause of the time effect may be that to form a metallic junction metal has to penetrate the protective layers e g the surface layers of oxide, which exist at the interface and that this penetration takes time to reach completion It is unlikely that these results are due to air trapped between the colliding surfaces because experiments carried out *in vacuo* also show that there is much greater adhesion under static conditions This dependence of the adhesion upon the time of contact is probably closely related to, and may help to account for, the variation of the coefficient of friction and of mechanical wear with speed

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A New Virus Affecting Mangolds, Sugar-beet and Related Plants

WHILST making routine inoculations from seed mangolds affected with sugar-beet mosaic an apparently new virus came unexpectedly to light There are one or two unusual facts about this virus which make it interesting So far, all attempts to induce it to become systemic in its host plant, including the mangold, have failed In this respect the virus resembles the tobacco necrosis viruses which also, as a rule, do not become systemic in their host plants and like this virus, produce large numbers of necrotic lesions on the inoculated leaf

In experiments with the virus from mangolds it has been found that the red beet is the most susceptible host and reacts with the formation on the inoculated leaf of large numbers of local lesions, see *Figure 1* The virus also produces local lesions on sugar-beet, spinach-beet, mangold, New Zealand spinach and a miscellaneous group of plants such as cabbage, broad bean, French bean and several solanaceous plants In all these plants, with the possible exception of the French bean, no systemic spread of the virus in its host plant has been observed Yet presumably the virus must have been systemic in the original mangold plant from which it was first isolated There is no information at present on how the virus spreads in nature, if it does spread Experiments to find out if the aphids commonly found on mangolds and sugar-beet would transmit the virus have so far proved negative This may be, in part, due to the fact that the insects are unwilling to feed on the necrotic tissue in which the virus is contained

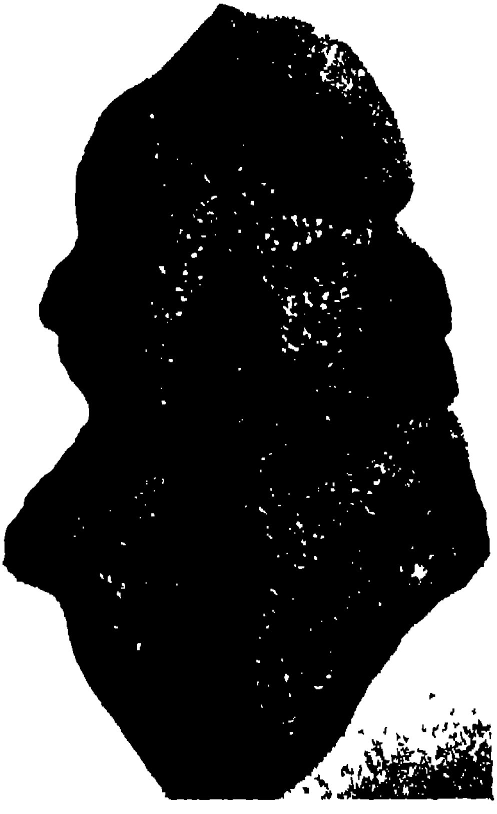

Figure 1 Leaf of red beet inoculated with a new virus from mangolds note the large number of necrotic local lesions

The very large number of local lesions formed by the virus on the inoculated leaves suggests that it is present in fairly high concentration and this is further borne out by the dilution end-point which is 10^{-6}

It is not very likely that this virus will prove to be of much economic importance but its properties, some of which have been briefly outlined here, suggest that it may be of considerable scientific interest

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Creep Deformation of Metals

Two features of the creep of metals which have aroused interest of late are *1* effects of recrystallization and grain growth, and *2* formation of subgrains similar to those seen in the phenomenon described as polygonization[1]

Metallurgists have long been aware of the fact that increases in the rate of deformation may occur when recrystallization or grain growth proceeds in a metal[2] Interest has been stimulated in the subject by the recent observations of ANDRADE[3]

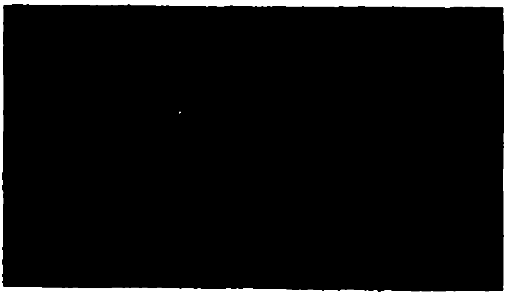

Figure 1 Magnification × c 1, reduced 5/7 on reproduction

We have recently encountered a number of spectacular cases of grain growth in aluminium ½ per cent silver alloy in which the effect on the creep rate was not very large A typical example is shown in *Figure 1* in which it will be seen that the small grains (about 0 5 mm diam) in the head of the specimen have become enlarged to a single grain of diameter almost equal to the specimen diameter (22 mm) This grain has drawn down and fractured as shown Typical test conditions leading to this grain growth are shown in *Figure 2* from which it will be seen that there is no considerable increase in creep rate before 130 hr and about 20 per cent total strain We were unable to obtain data at higher values of strain In another similar test we were able to continue the observations to 190 hr and nearly 60 per cent strain, and from 130 to 190 hr a slowly increasing rate of creep was observed which could be accounted for by the fact that the test was made at constant load and not at constant stress Fracture of the specimen occurred at 214 hr so that we can conclude that either the grain growth did not affect the creep rate substantially or the grain growth occurred in the last few hours of the test

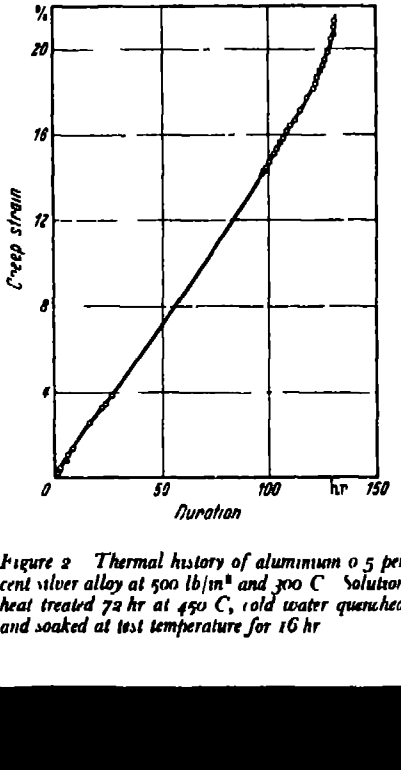

Figure 2 Thermal history of aluminium 0 5 per cent silver alloy at 500 lb/in² and 300 C Solution heat treated 72 hr at 450 C, cold water quenched and soaked at test temperature for 16 hr

Figure 3 Magnification × 3, reduced 1/2 on reproduction

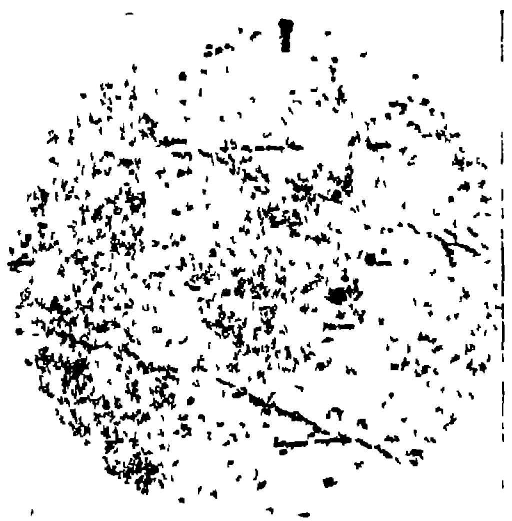

Figure 4 Magnification × 40, reduced 3/5 on reproduction

The surfaces of the large crystals formed in this way showed the familiar strain markings seen in *Figure 3* Crystal damage is apparent within the crystal on sectioning, running out to the surface on lines corresponding with the surface markings The type of damage is illustrated in *Figure 4* at a low power and at higher power in *Figure 5* This latter figure shows a resemblance to the polygonized structures due to straining and annealing which have been described by LACOMBE and BEAUJARD[4] or the structures due to creep as described by WILMS and WOOD[5] X-Ray observations on this structure show that there is a considerable difference in the orientation of subgrains in an area of say 1 mm² and in addition the units show considerable internal strain Bearing in mind the very rapid deformation which must have occurred immediately preceding fracture it seems likely that this will account for the distortion apparent in the subgrains, and that they are essentially units of the type observed by WILMS and WOOD

After fracture of the specimen a much more generalized breakdown into subgrains is observed as shown in *Figure 6*

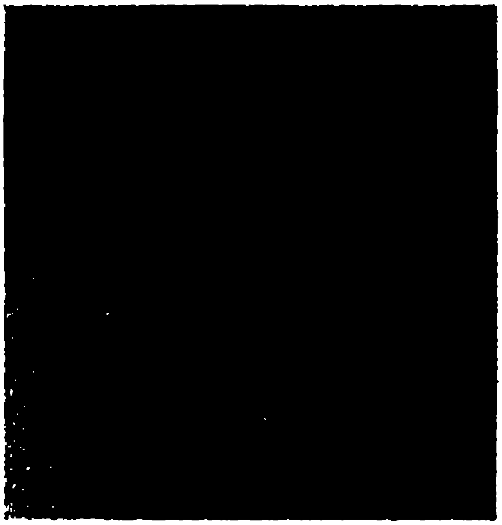

Figure 5 Magnification × *250, reproduced same size*

These observations suggest to us that the breakdown to subgrains is not the primary cause of creep but a secondary effect resulting from creep When a new volume of the large grain is formed it is probably free from strain markings on the surface and from subgrains internally This volume then deforms on particular planes by the usual glide mechanisms giving surface markings the number and spacing of which will depend on the temperature and stress as shown in the classical work of **Hanson** and **Wheeler**[6]

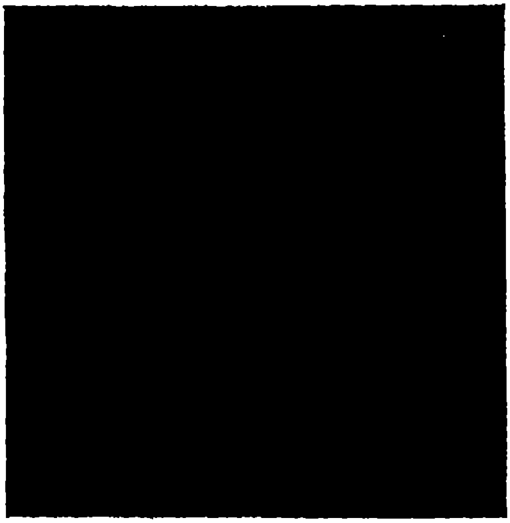

Figure 6 Magnification × *40, reproduced same size*

Subsequently the breakdown to subgrains proceeds in the heavily deformed regions only. Creep no doubt then proceeds on new planes leading to further subgrains until the crystal is completely broken down to subgrains The deformation must be substantial before this occurs however and although further deformation will probably occur by rotation of the subgrains it seems likely that this will be only a small proportion of the total deformation The process is therefore rather similar to that of local heavy deformation followed by annealing such as **Cahn** postulates as necessary for polygonization and could be explained in terms of dislocations This indeed was suggested by **Crussard**[7] in his discussion of the paper of **Wilms** and **Wood** and is consistent with recent observations made by **Greenough** and **Smith**[8] in a separate study in this laboratory

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(Received August 1950)

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Commentary:
Specialized Scientific Training and Citizenship

IT IS OFTEN IMPLIED, if not actually asserted, that a specialized scientific training necessarily means a narrow education and a limited cultural and philosophical outlook I believe that the exact opposite may and should apply. A general education does not consist of the knowledge of facts or of the acquisition of proficiency in many different fields It should be the means by which a person acquires wide human as well as deep intellectual interests, and whereby the personality is fully developed in the best sense This can be achieved by a right approach to specialization in a particular field, provided that the subject selected is studied in its correct setting with respect to knowledge in general, and to those human problems to which it may be applied.

Perhaps I may be forgiven if I illustrate my thesis by reference to the subject about which I know the most—Crystallography , a subject so specialized that most people do not even know what the name means, and suppose it either has something to do with fortune telling or is a branch of Theology Crystallography is the science that deals with the arrangements of atoms in solids. Originally it applied only to the external study of well formed crystals and was a branch of mineralogy and of geometry , but modern methods of investigation have shown that there is no real dividing line between obvious ' crystals ' and other solids such as massive metals or chemical powders The fundamental thing about them all is that their component atoms form a periodically repeating pattern, a pattern in three dimensions. The properties of solids depend not only on the kinds of atoms of which they are composed, but also on the arrangement of those atoms. Now solids are very common things , we handle them every day , they enter into every science and every industry ; we read them, write with them, buy and sell them, eat them and eat with them We are, of course, partly solid ourselves To know our subject thoroughly, therefore, specialized though it may be, we must know something of all the sciences, of humanity and industry in general, of ourselves and our physiology in particular. But we have also developed methods of studying crystal structure and the properties and behaviour of solids which use detailed experimental techniques common to other sciences, and the interpretation of the experimental data requires a considerable knowledge of and facility with advanced mathematics

Let us be more specific about the relationship of crystallography to the better known sciences We study the arrangement of the atoms by diffraction methods, but we find that these give us information not only about the positions of the atoms but also about their movements, not only about crystal structure but also about crystal dynamics. We become interested in the conditions of stability of a lattice, and about the transformations that may occur in it, including of course, melting or volatilization or surface changes. We find that our study of dynamics throws lights on questions of diffusion and of annealing. Since the movements of the atoms are dependent on the forces within the crystal we must study the elasticity , and we find also that many other important physical properties, such as ferromagnetism and piezoelectricity, are intimately related both to electron arrangement and to atomic periodicities All this is physics In the early days of x-ray crystallography the investigation of the mechanism of scattering and of x-ray emission, studied using a crystal as an analyser, threw considerable light on the structure of the atom Neutron diffraction by crystals is now providing data which should help to elucidate the structure of nuclei , we are involved in the study of ultimate particles , to be up to date in our subject we must keep in the forefront of modern nuclear theory Coming back to our atomic arrangements, it is clear that this lands us also right in the middle of Chemistry The chemist is, of course, intensely interested in the spatial arrangement of atoms in molecules and in the interatomic and intermolecular forces , in bond lengths and valency angles Crystal diffraction patterns can be used for identification and analysis, and they also allow us to study reactions in the solid state It is necessary to have a wide knowledge of chemistry in order to prepare crystalline compounds for investigation and, indeed, to know what problems merit detailed study and this applies in the inorganic and organic fields alike Chemical compounds, if solid at all, are necessarily crystalline, but so are many biological substances virus particles, globular and fibrous proteins, cotton, silk, rayon, hair, horn, teeth, wool, muscle, nerve These are, if not completely, at least partly crystalline , their atoms are not randomly distributed, they are periodically arranged in at least one direction and at least over small volumes Moreover, the fact that such substances as penicillin and DDT are very well crystallized materials brings crystallography into the field of the medical sciences from another angle The crystallographer, in fact, must know a good deal of mathematics, of physics (classical and modern), of chemistry, biology, of metallurgy and mineralogy, if he is to be really well grounded and up to date in his own subject The fact that he may be called upon to identify a portion of paint from an ' old master ' the authenticity of which has been called into question, or to analyse the deposit on an old Roman buckle will, if he is at all curious, direct his thoughts into channels less directly associated with everyday affairs But everyday affairs will certainly intrude themselves

He becomes interested in the structure, say, of the diamond, and in the relation of the structure to the properties of the diamond He learns that diamond drills were used in making the Simplon tunnel and that miles of tungsten wire for electric light bulbs are drawn through diamond dies In finding out how diamond dies are made he will be struck with the monotony of the work involved and he is at once caught up in a modern social problem He may well ask also how diamonds are mined, and if he does, he will be sure to come up against racial problems generally But once he begins to interest himself in the distribution of minerals in the earth's crust, Heaven help him ! He is involved in economics , he must realize how much national power and prosperity, how many national rivalries, depend on unequal possession of vital or rare minerals gold, silver, coal, lead, tin, iron, uranium, graphite or beryllium And he must be dull indeed if he merely notes these facts and passes them by without further thought or study

A study of the structure and formation of ice crystals leads to an interest in glaciology, in the flow of glaciers and the causes of frost-heaving, in meteorology, the formation of hail and the precipitation of clouds , together maybe with the legal problems involved when the farmers of one American State find that the snow which provides their water has been diverted to provide ski-ing for the rich visitors to another neighbouring State !

He will meet also the problems that confront countries which are dependent on hydroelectric power, when their winter supplies of rain or snow fail, their glaciers recede, and their rivers dry up as a consequence

There are crystals which are of interest to the historian because of their importance in industry and in the past economical life of the nations the trade in alum, for example, was once a monopoly of the Vatican, and it was used to provide revenue for the Crusade Fund* Prehistoric man can sometimes be dated, at least relative to his surroundings, by the amount of

*SINGER, C *The Earliest Chemical Industry* London, 1948 fluorine that has replaced the hydroxy-groups in his fossilized bone material The replacement is only possible because of the special pattern of the atoms in the bone structure Archaeology, the history of science, art, architecture, engineering, sociology, geography , none of these can be neglected by the crystallographer who wants to know his job thoroughly and who is intelligent enough and human enough to take an interest in the various side lines to his profession

NEED FOR CLEAR THINKING

But there is much more to it than that The specialist must be able to write down the results of his experiments clearly and intelligibly , he will probably also be called upon to explain them to audiences of non-scientists or of scientists in other fields He must develop a good style, and it is unlikely that he will be able to do this unless he studies masterpieces of good writing, and listens to good speakers himself It is to be regretted that this is so seldom realized by undergraduates, and that otherwise good students are often unable to write down logically and concisely what they have done and what they deduce from their observations Even experienced research workers sometimes seem to imagine that they must wrap up their investigations in long sentences and words that none but their colleagues can understand Let me quote in contrast a passage from a paper by W H Bragg

> ' There are three stages in the arrangement of matter the single atom as we find it in helium gas , the molecule as it is studied by the chemist , and the crystal unit which we now examine by x-ray analysis To take an example, there are the *atoms* of silicon or of oxygen The *molecule* of silicon dioxide contains one unit of silicon and two units of oxygen . Lastly, there is the substance quartz, of which the *crystal unit* consists of three molecules of silicon dioxide arranged in a special fashion which we now know has a certain screw-like character The quartz crystal contains an innumerable multiplication of these units Each of the units has all the properties of quartz and, in fact, is quartz , but a separate molecule of silicon dioxide is not quartz (*Concerning the Nature of Things*) '

Here you have the true specialist , the man who can dive deeply because he is the master of his medium, and who does so so gracefully that it seems easy

INTERNATIONAL INTERCOURSE

The scientist must of course be well read and be able to read critically and accurately in several languages other than his own He will be at a great disadvantage if he has to rely entirely on English abstracts of the world's scientific literature It is probable also that he will attend international conferences at home and also, perhaps, abroad , and he will find it both interesting and advisable to know something of the customs, economics, literature and history of the countries from which his foreign colleagues come If he travels abroad he will certainly soon know a good deal of the geography and of the agricultural and industrial development of other countries All good scientists, indeed, are internationalists and cosmopolitans

I think it is true that in order to be able to take advantage of the various opportunities for adult education provided by a specialist career, the scientist should not have specialized too soon The tendency today is for universities to set so high an entrance standard that boys and girls must study their special subjects intensively for at least two or three years before entry, especially if they wish to attain scholarship, standard Personally, I believe this to be quite wrong I would rather have a student who can think logically, who knows how to use a library efficiently, who has studied good writing and who can express himself clearly, concisely and stylishly on paper, who has a working knowledge of mathematical technique and of two or three foreign languages, and who has facility with tools, than one who has ' dropped ' everything at the school certificate level in order to concentrate on two or three subjects at university scholarship level, and who will probably in that way get quite a wrong idea of the objects of a university career, and of the state of his own knowledge Most of us, I should think, know men who, after taking one degree in, say, Classics or Mathematics, have decided to make a particular branch of Science their main professional study and who, in spite of little or no early scientific training, have done exceptionally well in Science I do not believe that they are in any way gifted beyond their fellow professionals who have been trained in science from their youth up It is simply easier to learn any specialized subject when logical thinking and correct ways of learning have become almost automatic

But, of course, the very process of learning to do one thing very carefully and thoroughly is itself a discipline I am considering particularly here the kind of specialization that includes a training in research I would like to quote Sir **William Bragg** once more

> 'Research work brings out a man's self-reliance and proves his capacity to march by himself It is a discipline to put the text-book to one side and to get out further knowledge by one's own effort It teaches the student how to value evidence how to read with discretion, since he must weigh what others have done before he uses the previous knowledge as a foundation for his own advances He learns to meet disappointment, to realize how little he can do in a day, and that weeks or months may go by without obvious progress It is all very humiliating, and the blunders one makes are very foolish, and the one redeeming feature is that in its apparent perversity it is like every other piece of real work Research is rather like playing against bogey at golf Nature never has any weakness of which advantage may be taken, there is no hole to be won by bad play because our opponent plays worse Yet research is very human and there is always the hope before every student that he may contribute something to the total of human knowledge Perhaps the hope is not so often reached as it might be, but that does not mean that the work has been done in vain a thousand times, no It is a remarkable fact that if a man tries to set down on paper, in line or in colour, that which he sees in Nature, his own vision of what is beautiful is quickened The pencil teaches him the beauty of line, and the brush opens his eyes to all sorts of delicate colour schemes which he never saw before It does not matter if his efforts are a bitter disappointment to himself, and he need not show them to any one else Similarly, the man who strives to understand the workings of Nature, by experiment which may make him feel very feeble and stupid, is paid by his discovery of a richer world There is a fellowship between all who have tried to understand, which enables the worker in one field to have a welcome power of appreciation of the work of others He gains not only in the richness of appreciation of what is beautiful and interesting, but also in the power of making friends'

DEVELOPMENT OF CITIZENSHIP

Now I contend that the man or woman who has had such a training ought to be not merely a better scientist, but a better citizen for it But that will only be so if he deliberately puts into practice, in everyday life, the ethics of the laboratory

Science itself may be, as so often is said, morally neutral, but that is not true of scientific inquiry, and it cannot be true of the scientist Complete honesty and integrity are essential to the research worker He cannot and must not adjust his results, or neglect to consider hypotheses other than those apparently proved correct by his experiments He must always be ready to admit error, indeed, he calculates its probability Mistakes in published work must be publicly corrected, never concealed for the sake of personal or national prestige Yet the same man who is so careful of his facts in the laboratory and who will go to endless pains to check his references is not always by any means so careful when it comes to repeating political rumours, quoting newspaper reports based on half truths, or distorting economic data in support of a non-scientific argument! Nor is he always willing to admit that the politicians of his own country, or of his own party, may have made mistakes although, in fact, politicians so seldom have all the data, and have to act so quickly, that their choice of action is never likely to be unbiased or impeccable

Michael Faraday, towards the end of his life, wrote thus of his failure to demonstrate any measurable relationship between gravity and other fundamental forces

> 'It might indeed have been anticipated from the very views I entertain, that we could

hardly hope to lay hold by experiment of such an amount of gravitating force as would yield appreciable evidence of electric or heat force but if we were to stop the first institution of experiment in any new direction for such a reason, what progress, or more, what discovery, could we hope to make by its means in any of the, as yet, undiscovered paths of science '

The scientist must be an incorrigible optimist ! He must not allow even reason to deter him from preserving an open mind, from being ready to try new experiments in the hope of finding new truths He must strive to remain free from prejudice, unbound by conventional ways of thinking , ready, as FARADAY wrote on another occasion, to ' Let the imagination go guiding it by judgement and principle but holding it in and directing it by *experiment* ' When the scientist reaches an impasse, as with the corpuscular *versus* the wave theory of light, then he must be ready to think on a new plane, to admit hitherto inadmissible hypotheses and to base experiments on them, in order to test their validity

I believe that it would be invaluable to the world if the scientist could carry over his training in this respect from the laboratory into the field of political thought and action and could infect his fellow men with the same attitude So often an admittedly ' ideal ' line of action is dismissed as impracticable and never tried, although all other lines of action are obviously disastrous. The result is a fatalism that paralyses initiative The kind of men the world needs most today are men who can plan and execute bold experiments experiments in the kind of international cooperation, of friendship, of openness and of complete disregard for considerations of national prestige, that are typical of Science at its best If such experiments do not succeed, at least they are hardly likely to land us in a worse state than we find ourselves at present. In the words of Dr BROCK CHISHOLM, formerly Director-General of the World Health Organization

> ' We are now in a new kind of world Man may or may not survive ; it depends entirely on his ability to change his behaviour pattern to meet changed conditions of living. To make these adjustments we must have new knowledge and it must be acquired by ourselves We would do well to begin with the assumption that all our ancestors have been wrong If their behaviour patterns are carried on by us for only a few more years, they will destroy the human race '

In the task of finding out how to live in the new world, scientists should be able to give a lead to their fellow citizens The instinct for self-preservation is strong, however, and I do not believe that the world will destroy itself What does seem likely is that the uneasy world of the future may be very different from the world that most of us would like to live in In spite of, or perhaps because of, a war fought to end Nazism and to preserve democracy, democracy as we know it is in danger of disappearing , and by democracy I mean the form of government that not only tolerates the existence of a critical minority, but that welcomes ' the Opposition ' and incorporates it into its political system Tolerance is only practised fully in times of real peace and of comparative prosperity When a state of war exists or threatens, when poverty, misery, dissatisfaction or economic difficulties prevail, then governments tend to become authoritarian

It is just at these times that the scientist needs to remember that he serves not only humanity but also his own country best by emphasizing the importance of freedom Scientists must uphold the fundamental right of all men ' to hold opinions without interference and to seek, receive and impart information and ideas through any media and regardless of frontiers ' Just as personal friendships and cooperation between specialist scientists of different nationalities have contributed largely to scientific progress, so also has the courage of those scientists who have stood by the results of measurement and deduction honestly and carefully made But it is clear that young people need careful education if they are to reach opinions in a free, honest and disinterested way , they should never be trained to unthinking obedience, but should rather learn how freedom and responsibility may be integrated in the service of truth and of mankind

K. LONSDALE

The Ultracentrifuge

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At the beginning of this century J. Perrin measured both the sedimentation velocity and the sedimentation equilibrium of large suspended particles in the gravitational field and thus introduced a new approach to the study of the kinetic properties of molecules. From the theory of equipartition of energy it was known that the study of colloids would yield information on the general molecular-kinetic theory and this appears to have been the main interest in such systems at that time. For some years gold sols or similar classical colloids were used for such investigations; since then, however, many more colloidal systems of biological and technical interest have been discovered and this has given a big impetus to the development of physical techniques. Though it is possible to measure the sedimentation equilibrium of large particles with a high density in the earth's gravitational field this becomes difficult or impossible for most organic colloids or macromolecules. The use of centrifugal fields was therefore adopted to increase the force acting on the particles in suspensions or solutions.

Centrifuges have been used for a long time in processes involving the separation of materials of different densities and the problem of separating small particles with densities differing only slightly from the suspension medium is merely one of increasing the centrifugal force $\omega^2 x$, where ω is the angular velocity and x the distance from the axis of rotation. If, however, the centrifuge is to be used for the measurement of either the sedimentation velocity or sedimentation equilibrium it is necessary to prevent convection due to temperature fluctuations within the cells and to have some means of observing the changes of the solute concentration in the centrifuge cell. Furthermore, the speed of rotation as well as the temperature of the cell must be known accurately for interpretation of the results.

The full derivation of the equations describing the behaviour of particles in a centrifugal field is given in the comprehensive book of T. Svedberg and K. O. Pedersen[1] and in many papers by Svedberg and his collaborators quoted therein. Only some of the final results need be given here so as to show the quantities upon which the sedimentation velocity depends and the information which can be obtained from its measurement.

The sedimentation constant s is defined by

$$s = \frac{dx}{dt}\Big/\omega^2 x \qquad (1)$$

and by

$$s = M(1 - V\varrho)/f \qquad (2)$$

where dx/dt = sedimentation velocity, f = frictional resistance, M = molecular weight, V = partial specific volume of the sedimenting particle and ϱ = density of the solvent.

For solid spherical particles the frictional constant can be calculated from Stokes law. On a molar basis

$$f = 6\pi r\eta N \qquad (3)$$

where r = radius of particles, η = viscosity of solvent and N = Avogadro number.

The molecular weight can therefore be calculated from the sedimentation constant only if the molecules are spherical and unsolvated, or the frictional constant is determined independently from diffusion measurements. The diffusion constant is

$$D = RT/f \qquad (4)$$

Therefore from equations 2 and 4

$$M = \frac{RTs}{D(1 - V\varrho)} \qquad (5)$$

Besides giving information about the molecular weight, the combined data from diffusion and sedimentation experiments also enable one to draw some conclusions about the shape and solvation of particles. It is, however, difficult to differentiate between these two effects on the frictional constant. J. L. Oncley[2] discusses this problem in some detail.

In 1923 T. Svedberg and J. B. Nichols carried out their first experiments with an electrically driven 'optical' ultracentrifuge at the University of Wisconsin and when Svedberg returned to Uppsala in 1924 he continued to develop these for the study of sedimentation equilibria. Gold sols were used as the first test object and in the following year T. Svedberg and R. Fahraeus carried out ultracentrifugal experiments with protein solutions. The great importance of proteins, which hold key positions in almost all biological processes, encouraged the Swedish workers to start a big programme of research which yielded invaluable results on the composition, molecular weight and weight distribution, as well as on the shape and structure of many protein systems. Most protein molecules sediment relatively slowly by colloidal standards, and in the centrifugal fields produced in 1924 only sedimentation equilibria could be measured. In 1927, however, T. Svedberg and T. Lysholm built an ultracentrifuge with an oil turbine drive which could develop a centrifugal field equivalent to 100,000 *g*. Thus it became possible to study the sedimentation velocity of proteins of molecular weight as low as 50,000. A very important result of the ultracentrifugal studies on protein solutions was the discovery that these substances are fairly homogeneous molecular entities and not random aggregates like colloidal gold or similar systems. Though quite a number of investigations on other biocolloids (glycogen, nucleic acids *etc*) and synthetic high polymers have been carried out in the ultracentrifuge, certainly most of the work was done on protein systems. The large number of valuable data of biochemical interest which could be obtained probably delayed somewhat the further development of the physical aspects of the method.

Further historical and technical information about the development of the ultracentrifuge and the investigations carried out prior to 1940 can be found elsewhere[1, 2].

DEVELOPMENT OF ULTRACENTRIFUGES

For the three purposes of measuring sedimentation constants, sedimentation equilibria and preparative centrifugation different machines were built, though it is now possible to construct a centrifuge which will serve all of them. At present oil turbines, air turbines and electrical motors are being used as alternative driving mechanisms. The oil turbine machines are not manufactured outside Sweden and the two models which are in England (at the Biochemical Laboratory, Oxford and Lister Institute, London) were the first, and for some time the only, ultracentrifuges in this country. Though such accessories as the optical system, speed measurement and temperature control have been modified at Oxford in order to increase the accuracy and simplify the procedure of sedimentation velocity measurements, the design of the drive, rotor and centrifuge proper have not been changed from that previously described[1]. In the Svedberg oil turbine model the rotor spins in an evacuated steel chamber, with its axis of rotation horizontal. Provision for optical observation is similar in all the centrifuges; the cell has transparent endplates and windows are mounted in the steel chamber in appropriate positions. In electrically and air driven ultracentrifuges the axis of rotation is, however, vertical and the optical arrangement has to be varied accordingly. The Svedberg oil turbine ultracentrifuges are used for the determination of sedimentation velocity and analysis of homogeneity only, but in these lines they have certainly provided the bulk of the reliable information so far obtained.

The construction of air turbine ultracentrifuges for use as analytical and measuring instruments as well as for the preparative separation of macromolecules began soon after Svedberg's successes with the oil turbine. The machines driven by compressed air are considerably simpler and cheaper to build and were therefore more widely adopted. The compressed air is used to support the air turbine as well as to drive it, and the rotor spins horizontally on a thin spindle leading from the turbine through an oil leak into the vacuum chamber to the rotor. On account of simplicity of drive and bearings this arrangement is very widely used for preparative centrifuges in virus work. The range of size of virus molecules is such as to make this technique very useful for their separation from other solutes.

As already mentioned an electric drive was used for the very first ultracentrifuge built by Svedberg and Nichols, a low speed machine yielding a centrifugal force of about 10,000 *g*, but this was sufficient for the determination of sedimentation equilibria and moreover the drive through a frequency controlled motor was particularly suitable for this purpose as running at constant speed for periods of several days was required. The technique of sedimentation equilibrium measurement was, however, not widely adopted outside Uppsala, and neither the method nor its results[1] will be discussed here. The further development of electrically driven ultracentrifuges was rather neglected until E. G. PICKELS recently constructed an instrument which can be used for all three purposes: measurement of sedimentation velocity, sedimentation equilibrium and preparative centrifugation. This machine is again very much more costly and more elaborate than the air driven types, but it has many automatic devices which make for easy routine experiments. The drive motor is air and water cooled.

The smaller the rotor the greater the centrifugal forces which can be developed without danger of fracture due to failure of the material. Small steel balls a few millimetres in diameter have been spun, suspended in a magnetic field, at a speed of 10^6 r.p.m. For the purpose of measuring sedimentation velocities it is, however, desirable to have the cell at as great a distance from the axis of rotation as possible so that the force gradient is not too large through the length of the path of sedimentation and negligible over the width of the boundary. The column of solution in the cell should be of the order of 1·5 cm high, so that even fairly rapidly diffusing substances can be observed during a course of sedimentation when the boundary is free from the meniscus and the 'leading tail' is not affected by back diffusion from the bottom of the cell. If the distance from the axis of rotation to the centre of the cell is 6·5 cm the distortion of the boundary due to a gradient of the centrifugal force over say ± 2 mm from the centre of the boundary will not be too serious. These dimensions for rotor and cell have now been almost universally accepted as the most suitable and are used for the construction of the three commercially available machines For rotors of total diameter about 18 cm, the maximum speed for prolonged running is about 60,000 r p m The centrifugal force at 6 5 cm from the axis of rotation is then about 250,000 *g* The rotors are usually forged from steel or duraluminium

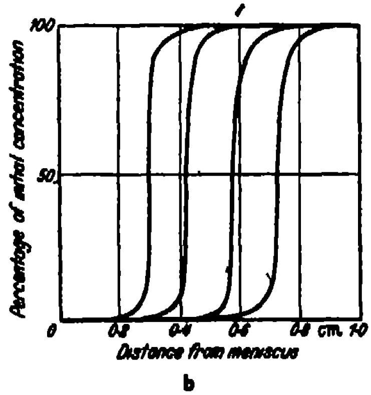
There is now no significant difference between the various designs for cells in centrifuges which are producing accurate results and they can be used both for measurement of constants and analysis of homogeneity The cavity in the centre, into which about 1 ml of the solution is sealed, is sector shaped A dummy balance cell is housed in a second hole provided in the rotor, and the complete assembly has to be tested for static and dynamic balance

Preparative rotors can be fitted on the air driven and electrically driven centrifuges Of the order of 100 ml of solution can be subjected to centrifugal forces of about 100,000 *g* Some more recent constructions allow even larger quantities of solutions to be subjected to still greater centrifugal forces Special preparative ultracentrifuges are of course available, no arrangement for optical observation and the provision for only approximate speed and temperature measurement are required for such machines

OPTICAL OBSERVATION OF BOUNDARIES AND CALCULATION OF SEDIMENTATION CONSTANT

Methods for the optical observation of boundaries due to concentration gradients in liquid systems were developed simultaneously for the measurement of sedimentation velocity, electrophoretic mobility and rate of diffusion Two principles have been employed for this purpose, one involving the change of light absorption, the other the change of refractive index with solute concentration The light absorption method is useful for the study of some coloured solutions which do not allow sufficiently intense and uniform transmission of light of any wavelength, within the visible spectrum, for the use of one of the refractive index methods Under suitable conditions the latter are, however, considerably more accurate and are therefore used whenever possible With the light absorption method a plot of the concentration against distance from an index mark is obtained from photometric measurements across the photograph of the liquid column An example of this procedure is shown in *Figure 1*

Methods for optical observation of refractive index gradients were already known towards the end of the last century but were only adapted for the observation of moving boundaries during the past twenty years Among these methods are several which make use of interference phenomena and though some of them are now employed for the accurate determination of diffusion constants they are not at present used for the observation of sedimenting boundaries The scale method was first recommended for ultracentrifugal investigations by O LAMM in 1928 and it soon replaced the light absorption method in the Uppsala laboratory If a scale is placed between a light source and an ultracentrifuge cell, or other column of solution, and the camera focused on this scale the scale lines are displaced by a concentration gradient in the cell The scale line displacement is proportional to the concentration gradient (refractive index gradient) corresponding to the position of each individual line *Figure 2* shows an example of a sedimentation diagram obtained from a plot of scale line displacement in scale *A* from the reference scale *B* against distance from an index mark *Z* Scale *B* is obtained from a photograph of the cell filled with solvent only and therefore represents an optically homogeneous column The distortion in *A* between the lines 40 to 70 can be seen readily In practice the scale line displacement is measured under a microscope This procedure, though very accurate, is rather tedious and this disadvantage has led J ST L PHILPOT to


a

b

Figure 1 *Sedimentation pictures* a *obtained by means of the absorption method, and curves of concentration distribution* b *for the haemocyanin from Helix pomatia at* pH 5 5 (*M* = *6,600,000, s* = *98 9* × *10*$^{-13}$), *centrifugal force 45,000 times gravity, time between exposure 5 minutes* (*reproduced from Svedberg and Pedersen*[1])

develop an optical arrangement which gives directly a curve representing a plot of dn/dx against x (where dn/dx is the refractive index gradient) on a ground glass screen or a photographic plate This system, which is a combination of the Thovert principle with the schlieren method is described in great detail elsewhere[4, 5] There is some difference of opinion about the relative merits of using a tilted slit, bar or edge with these methods but there is probably not very much to choose between them The present author prefers the tilted edge, giving a picture as in *Figure 3*, for accurate measurements of sedimentation constants, though it may be easier to detect the separation of a small secondary boundary from the main one when a tilted slit is used In the latter a bright curve is seen over a dark background on the photographic positive By whichever method graphs of dn/dx against x are obtained, the measurement and interpretation of the sedimentation diagrams remain the same The sedimentation constant s is calculated from measurements on successive photographs of the distance of the midpoint of the boundary from an index mark and is usually expressed as $s_{20} \times 10^{13}$ cm/sec/dyne The integration of the curve gives an estimate of the amount of sedimenting material responsible for each individual boundary, and thus yields interesting analytical information about the solution under examination But for diffusion occurring simultaneously with the sedimentation process, the boundary would of course be perfectly sharp Ideally the sedimentation diagram for the boundary of a homogeneous substance should therefore be a Gaussian curve with a second moment $\sigma^2 = D/2t$ where D is the diffusion constant of the substance and t the time for which diffusion occurred Unfortunately it is very difficult to make adequate corrections for all the perturbations, and the use of sedimentation diagrams for the calculation of diffusion constants can therefore only yield very approximate data This is a particular drawback for the investigation of the homogeneity of a substance as the superimposition of a diffusion curve upon the sedimentation diagram does not give an accurate picture of the amount of heterogeneity with respect to particle weight, though it does give some indication

A different procedure for the calculation of the sedimentation constant has to be adopted if the molecular weight of the substance is so small that a clear boundary cannot be formed within the length of the sedimenting path under the centrifugal force which can be developed Analytical procedures for the determination of the amount of material sedimenting across a plane in the cell have been suggested[1], and more recently H GUTFREUND and A G OGSTON[6] have described the calculation of the sedimentation constant of some polypeptides from optical observations

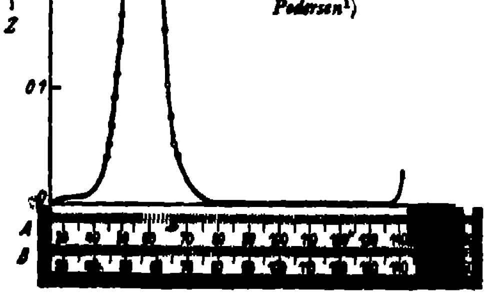


Figure 2 Illustration of the relationship between the scale image and the sedimentation diagram
(Reproduced from Svedberg and Pedersen[1])

Figure 3

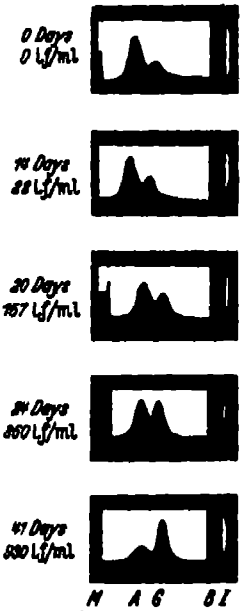


Figure 4

Figure 3 Sedimentation diagram from an ultracentrifuge run on 1 per cent solution of lactoglobulin Exposures, at intervals of 20 minutes, were taken with the Philpot optical system on the Oxford centrifuge and were kindly provided by A G Ogston

Figure 4 Ultracentrifuge diagonal schlieren photographs of sera from the horse 'Patrol' during immunization with diphtheria toxoid M, meniscus, A albumin, G, globulin, B, cell bottom, I, index (reproduced from Kekwick and Record[5])

SPEED AND TEMPERATURE MEASUREMENTS ACCURACY OF SEDIMENTATION CONSTANTS

The table of sedimentation constants and molecular weights of proteins which is given at the end of Svedberg and Pedersen's book gives much valuable information Many more proteins as well as other biocolloids have since been isolated and characterized by this method and it is almost a routine procedure now to follow the fractionation of enzymes and similar biologically active macromolecules by ultracentrifugal analysis From this point of view great accuracy is not required, but if exact information about size, shape and hydration of homogeneous (crystalline) proteins is sought for adductions to the molecular structure, very precise data are then required

The first attempt to determine the sedimentation constant of a protein with an accuracy of 1 per cent was carried out by H Gutfreund and A G Ogston[7], in their study of insulin solutions The discrepancies found between their results and some earlier work, carried out in Sweden and the U S A, led R Cecil and A G Ogston[8] to study the accuracy of ultracentrifugal measurements in some detail They have found that values for the sedimentation constant 'reproducible to 0 5 per cent, and probably accurate to the same limits, can be obtained if the conditions of running are standardized, if care is taken over measurement of the various quantities concerned, and if correction is made for error of measurement of the temperature of the cell contents'

In the Oxford laboratory the reed frequency meter, normally used for the speed measurement with the oil turbine ultracentrifuge, was supplemented with a frequency bridge to achieve the necessary accuracy of 0 1 per cent With this equipment one can measure the frequency of the alternating current whether generated by the magnetized rotor or by various other arrangements dependent on the revolution of the rotor With the new electrically driven centrifuges it is claimed that the speed can be kept constant automatically to within 0 1 per cent, the oil and air driven types of centrifuges can be adjusted to keep constant to within 1 per cent under suitable conditions

The temperature of the solution has to be recorded to within about 0 3°C and it is necessary to ascertain any discrepancies between the readings of the thermocouple near the rotor and the temperature in the cell Studies of this problem as well as of the accurate adjustment of the optical system and a way of calculating the sedimentation constant, making fullest statistical use of the measurements, have been described by Cecil and Ogston

APPLICATIONS

It is difficult to review adequately the results obtained with the ultracentrifuge without a detailed discussion of the theory of solutions, and only a general indication of some of the applications will therefore be given Some of these have, of course, already become self evident during the foregoing descriptions.

The sedimentation diagrams obtained during an ultracentrifuge run can show either a single homogeneous boundary, *Figure 3*, two or more separate homogeneous boundaries, *Figure 4*, or a heterogeneous boundary which is much wider than could be accounted for by diffusion alone The latter can either be the result of several distinct but unresolved components of slightly differing sedimentation rates or of a polydisperse system of random aggregates

Much interesting information about the composition of biological systems and changes occurring during certain biological processes has been obtained An example is given in *Figure 4*, showing the results obtained by R A Kekwick and B. R Record[9] in their study of the change in the composition of horse serum during immunization with diphtheria toxoid

The amount of the lighter albumin fraction decreases and that of the heavier globulin fraction increases with rise of antitoxin concentration in the horse serum It is interesting to note here that the globulin fraction which appears as a single boundary in the sedimentation diagrams can be resolved into several fractions electrophoretically

As previously stated, approximate sedimentation constants are known for almost all proteins which have been isolated, but a really careful study of these as well as related molecular constants is available for only a few Insulin and β-lactoglobulin have been most carefully investigated and similar investigations undertaken over a range of concentrations and in a variety of solvent buffers ought to be carried out on various derivatives of haemoglobin and serum albumin from different species, these proteins having been studied most extensively by all other physical methods[10]

The sizes of many viruses have been calculated from ultracentrifugal measurements and especially in the study of plant viruses, some of which can be obtained in crystalline forms, a great deal of accurate physical data have been obtained

The difficulties of obtaining reliable information about the shape and solvation of particles are multifarious, even when accurate data for the sedimentation constant and molecular weight, and from these the frictional force, are available

Some independent method has to be found to determine either shape or hydration alone before conclusions about the other can be deduced from the sedimentation constant. For proteins it is possible that data obtained from x-ray crystallographic investigations[11] will give really accurate information about shape and hydration, and will thus afford a useful check on the attempts to interpret frictional data[10]

Natural and synthetic high polymers of industrial importance are being widely investigated, and the results correlated with mechanical properties The study of the molecular weight distribution is of general interest and the ultracentrifuge has contributed much information in this line The molecular weight calculated from the diffusion and sedimentation constants represents a weight average (this is not strictly correct, a true weight average will only be obtained if the analytical method is used for the calculation of the constants) , from thermodynamic methods one obtains a number average molecular weight , and the ratio of the two values for the molecular weight is a measure of polydispersion G Herdan[12] discussed this problem in some detail and gives further references to work on molecular weight distribution

In conclusion the author may be allowed to speculate about an application of the ultracentrifuge which has occupied his thoughts recently the study of low molecular weight electrolytes The determination of thermodynamic activities of ions in the equilibrium centrifuge has been described by K O Pedersen[13], and studies of galvanic cells and the determination of transport numbers, which were suggested by R C. Tolman in 1911, have been taken up again more recently by D A MacInnes, and the results up to date are described by D A MacInnes and B R Ray[14] It would be of great value if sedimentation constants of simple electrolytes such as sodium chloride and potassium chloride could be determined really accurately, and there seems every hope that this can be done with some modification of the method used by H Gutfreund and A G Ogston[6] The use of the self-plotting interferometric optical system described by J St L Philpot and G H Cook[15] might afford a way of both simplifying and improving the accuracy of this procedure

The results of such investigations would be interesting for comparison with diffusion studies on electrolytic solutions and would help to evaluate the frictional force in transport phenomena in such systems

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Ion Exchange Resins in Chromatography

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MODERN developments in ion exchange materials date from the pioneering work carried out at the Chemical Research Laboratory at Teddington by B. A. Adams and E L. Holmes[1] in 1935 Little more was published before 1939, however, and it is in the last three or four years that ion exchange has attracted widespread attention New applications, new modifications of earlier ones, and new exchangers with improved or novel properties have followed each other in rapid succession, and it is safe to say that this stage of vigorous and rather confused advance is by no means over, for many potentialities of synthetic exchangers have not yet been exploited

In the field with which we are concerned here, namely the separation of closely similar substances by ion exchange columns, the most spectacular success has been the complete separation of the rare earths in America[2], as part of the Plutonium Project All the rare earth metals have been made available in pure form, several in kilogram quantities, and new standards of purity have been established In another field, the preparation of the pure amino acids from protein hydrolysates[3] is hardly less striking A characteristic feature of ion exchange columns which these examples illustrate is that they combine the extraordinary selectivity of chromatographic procedures with a much higher capacity than is possessed by the surface adsorbents of normal chromatography

Theory has not yet overtaken practice, but for all that there are several principles available to prompt and guide research, and an attempt is made to present these in the following pages The fundamental properties of ion exchange resins and the various procedures of chromatography must first be reviewed

PROPERTIES OF ION EXCHANGE RESINS

Resins[4] are usually classified as cation exchangers and anion exchangers A typical cation exchanger is the *Zeo-Karb 215* used by S M PARTRIDGE[3] This is a phenol formaldehyde resin carrying sulphonic acid groupings When immersed in water the resin swells , the amount of cross linking is sufficient to prevent its solution but insufficient to prevent rapid diffusion of solutes into and out of the resin , it can be modified somewhat in manufacture according to the use to which the resin is to be put

If a sample of the resin is shaken with a salt solution an exchange of cations occurs and a state of equilibrium is soon reached

$$\mathrm{R\ SO_3^-\quad H^+ + M^+ + Cl^- \rightleftharpoons R\ SO_3^-\quad M^+ + H^+ + Cl^-} \qquad (1)$$

The exchange has been looked upon as a reversible reaction and described by a mass action constant[5, 6], as an adsorption phenomenon to which one of the common isotherms may apply[7] , as a problem in the behaviour of ions at a charged surface[8, 9], or as a simple distribution between two homogeneous phases[10] These various analogies with other fields have much in common, but they are not identical in all their implications, and the present uncertainties show the need for more detailed experimental work Most of the data so far available for cation exchange have been given as values of K in the equation

$$\frac{[\mathrm{M_1}]_R}{[\mathrm{M_2}]_R}\cdot\frac{[\mathrm{M_2}]_S}{[\mathrm{M_1}]_S} = K \qquad (2)$$

where $[\mathrm{M_1}]_R/[\mathrm{M_2}]_R$ is the ratio of the quantities of the two cations retained by the resin, and the other terms are the concentrations in the equilibrium solution Where the two cations have different valences the exchange is in chemical equivalents, and if the suffixes 1 and 2 represent uni- and bi-valent cations the equation becomes

$$\frac{[\mathrm{M_1}]_R^2}{[\mathrm{M_2}]_R}\ \frac{[\mathrm{M_2}]_S}{[\mathrm{M_1}]_S^2} = K \qquad (3)$$

where $[\mathrm{M_1}]_R$, $[\mathrm{M_2}]_R$ are again the amounts of the two cations associated with a fixed quantity of resin A consequence of equation 3 is that the preferential adsorption of the higher valence ion is favoured at high dilutions, an important principle In the limited series of experiments so far reported the K values obtained are roughly constant when they refer to exchanges between ions of equal valency, but otherwise K may show quite wide variations[11]

So far the salt solutions have been regarded as completely dissociated, and if this is true the anions present can be disregarded, as an approximation If the salts are not completely dissociated this will naturally affect the exchange and, even if no other complications arise, the $[\mathrm{M}]_S$ terms must be given the values of the true ionic concentrations As an example, the bivalent metals are less readily taken up from their sulphate solutions, in which ionic association is considerable, than from their chlorides[6] Of the other side of the picture—incomplete dissociation in the resin—little is known, but a study of this will undoubtedly be of vital importance for future theory Carboxylic acid resins show a strong selective adsorption of copper, and it is surely no coincidence that the copper salts of the common carboxylic acids are abnormally weak[12]

Anion exchange has been less thoroughly studied than cation exchange but does not appear to involve any fresh considerations The usual classification into cation and anion exchangers is less helpful than a classification (on the basis of the free acid or basic form of the resin) into strong electrolyte exchangers and weak electrolyte exchangers The strong type exchangers so far discussed include *Amberlite IR 105* and *120* and *Dowex 30* and *50* (sulphonic acid groups), and *Amberlite IRA 400* and *Dowex 1* and *2* (quaternary nitrogen groups) Weak type exchangers include *Deacidite* and *Amberlite IR 4B* (amines) and *Amberlite IRC 50* (carboxylic acid) Many of the earlier exchangers contained groups of both types *e g* sulphonic acid and phenolic, but the present tendency is to use unifunctional exchangers as their behaviour is simpler both in theory and practice

The outstanding characteristic of weak resins is that the number of ionized groups, and therefore the exchange capacity, depends markedly upon conditions, and particularly on the *p*H of the solution Thus a weak amine resin will be highly ionized and its exchange capacity will be high in acidic solutions, but at greater *p*H's it will be largely unionized and inert With certain qualifications it can be assumed that these changes will be governed by the usual dissociation equilibrium for a weak electrolyte *e g*

$$RNH_3^+ \rightleftharpoons RNH_2 + H^+ \qquad (4)$$

and the theory of common ion effects, neutral salt effects and so on can be taken over from the ordinary theory of weak electrolytes An important difference, however, is that the RNH_2 on the right hand side of equation 4 is part of a structure carrying a high positive charge, and on account of electrostatic repulsion the hydrogen ion at the resin surface is not at the concentration registered in the remote solution, but at perhaps one hundredth of this value The same conclusion can also be reached by regarding the resin as a homogeneous phase and applying the Donnan membrane theory An amine resin in contact with hydrochloric acid will then appear as follows

Resin phase		Solution
RNH_2	H^+ (0.0014M)	H^+ (0.1M)
RNH_3^+ (7M)	Cl^- (7.0014M)	Cl^- (0.1M)

The concentration of chloride in the resin must balance both the RNH_3^+ and the H^+, and at the same time equilibrium requires the equality

$$[H^+]_R[Cl^-]_R = [H^+]_S[Cl^-]_S \qquad (5)$$

A more exact treatment would require large activity corrections If the resin possessed 7 milliequivalents of ionized groups per ml when in contact with 0.1M HCl, the concentrations would be as displayed in parentheses

Other important factors in the use of weak resins are that processes involving a change in the extent of ionization are much slower than those of simple ion exchange, and usually involve much larger swelling changes A distinction must therefore be made between their use for purely exchange reactions, carried out at a constant controlled *p*H, which, like similar reactions with strong exchangers, will be rapid, and those much slower processes in which an acid/base reaction is used—as when an acid is adsorbed on a basic resin and the anion then displaced by increasing the *p*H

CHROMATOGRAPHIC PROCEDURES

The term chromatography is now applied to any process in which a separation, or partial separation, is brought about through the relative motion of two phases In the field under consideration, a solution is passed through a column of the swollen resin Each constituent of the solution may then pass through the column with the same velocity as the solvent (if it is unaffected by the resin), with zero velocity (if it is firmly held by the resin), or with any intermediate value A successful separation will depend on the different solutes travelling at sufficiently different rates The retardation produced by the resin may be due to a variety of causes, acting together or separately In addition to ion exchange, molecular adsorption may occur in significant amounts on the resin framework , and a separation procedure may depend not only on exchange or adsorption equilibria but on the rates at which the processes occur A possibility now being actively followed up is the preparation of resins so closely cross linked that the exchanging centres are inaccessible to large ions, and the separation of small from more complex ions may utilize this fact Many other possibilities are still unexplored, for example partition chromatography on ion exchange columns, the use of mixed solvents, and the preparation for special purposes of resins containing highly specific groups

In general, there are two ways in which chromatographic columns have been utilized In the first, the solution is continuously fed into the column in an amount exceeding its total capacity The least retarded solute appears first in the effluent, but once the second solute has reached the end of the column any remaining solution would emerge as a mixture An enrichment or a partial separation can be achieved in this way in a substantial amount of mixed solute, and a multi-stage system has been described[13] which is capable of the large scale separation of two solutes This may be called the break-through method

In the other, the method of elution, a very much smaller quantity of solute is used but the separative powers of the column are exploited to the full This is the classical method of chromatography, in which a small quantity of material is adsorbed at the top of a column of suitable adsorbent, and the separate solutes washed down the column at different rates by means of a suitable solvent, or succession of solvents In especially favourable instances a solvent may be found which elutes only one of the constituents, and the remainder can then be collected in separate fractions by the use of more powerful solvents This will rarely arise with ion exchangers, where the aqueous solutions used as eluants can seldom exert such a highly selective action, and where the aim will be to choose conditions such that the solutes move down the column at markedly different rates, so that there will be a minimum of overlap of the various solutes in the effluent The theory of elution procedures has been developed by a number of authors[14] to a point where insight into the general process has been gained, and where semi-quantitative agreement between theory and experiment has been obtained in favourable circumstances, but it will be realized that a quantitative theory requires a knowledge of the adsorption equilibrium for each solute in the presence of varying amounts of other competing substances, and that if this information cannot be expressed in a simple equation, the formulation soon becomes impossibly complicated It must also be recognized that flow through a column is not exactly controllable and reproducible, and disturbances such as those caused through distortion of a theoretically horizontal boundary can explain a large margin of error between theory and practice

A very important modification of the elution procedure is the method of 'displacement development' due to A Tiselius[15] The mixture is adsorbed at the top of the column and developed by a solution containing a substance more strongly adsorbed than any in the mixture If the column is sufficiently good to effect a complete separation, the solutes will normally emerge from the column in separate zones, followed by the pure developer The abrupt changes that occur in some characteristic property as one zone succeeds another can be used to follow the process and to identify the constituents

SEPARATION OF ISOTOPES

T I Taylor and H C Urey[16] were the first to attempt the separation of isotopes by ion exchange On passing lithium chloride through a column of a sodium zeolite, the sample first coming through was enriched in the ^{7}Li isotope In other experiments a sample of lithium chloride adsorbed at the top of the column was eluted with sodium chloride, and again the leading sample had a high, and the tailing sample a low, $^{7}Li/^{6}Li$ ratio Long columns were used, but the grain size and the rate of flow were both too great to give equilibrium conditions E Glueckauf, K H Barker and G P Kitt[14] have continued the work on lithium isotope separation using very finely ground resin and slow rates of flow The first effluent was almost pure ^{7}Li, but the total amount of enrichment was disappointing, and far smaller than theory would predict Possibly too high a fractionation factor was used in the calculations, but in such a searching test of the theory disturbances in the column could also lead to a large discrepancy between theory and experiment

No other work on isotope separation has yet been reported except for some preliminary measurements of T I Taylor and H C. Urey[16] in which they extended their work to the potassium and ammonium ions With these the heavier isotope is preferentially held by the resin, the degree of enrichment obtained was again poor

In all these experiments the enrichment is due to a preferential adsorption of one isotope. The effect can never be expected to be large With lithium, which is probably very favourable, the equilibrium constant given by Taylor and Urey for the reaction

$$^{7}LiR + {}^{6}Li \rightleftharpoons {}^{6}LiR + {}^{7}Li \quad . \quad (6)$$

is 1 022 The only ways in which this figure might be improved are by varying the resin or the solvent No work has yet been reported on non-aqueous solvents, but there are grounds for believing that the choice of resin is important It has been stated that zeolites are more selective than the common resinous exchangers, and that the selectivity of the latter is improved by increasing the extent of cross linking[17]

An improved separation would also result if the efficiency of the column could be enhanced by an increase in the number of successive adsorption and desorption steps per unit length of column When a lithium salt solution is admitted to a column of exchanger in the sodium form, there will not be an immediate quantitative exchange, indeed, the exchange equilibrium favours a retention of the sodium on the resin Some of the lithium salt solution will therefore pass through the first layers of resin without undergoing exchange, moreover, the sodium gradually liberated at the top of the column will compete with the lithium, and reduce its adsorption lower down, and this loss of efficiency is repeated throughout the column It would seem better therefore to devise the experiment so that exchange was quantitative throughout, and this might be done by using, say, lithium acetate and employing a cation exchanger in the hydrogen form The acetate ion, by maintaining a high *p*H, would ensure that the exchange of lithium for hydrogen was virtually quantitative at all points in the column The same choice of reagents in an elution experiment would ensure that the material applied to the column was initially held in the narrowest possible band at the top of the column This principle, of employing weak bases or weak acids in conjunction with strong acid or basic exchangers, is of very general application

One further possibility of improving the separation is by supplementing the selective action of the resin by a chemical reaction of some sort in the solution phase In the case in point, where ^{6}Li is preferentially held by the resin, an increased separation factor would be achieved if the solution contained, either as the anion accompanying the metal or as an additional reagent, a material which combined with the lithium ion and did so preferentially with the ^{7}Li isotope, thus favouring its escape from the column

SEPARATIONS OF WEAK ELECTROLYTES

In biochemistry and organic chemistry separation problems will usually be concerned with weak electrolytes or their salts, and ion exchange resins are well adapted to deal with these The separation of two weak bases, B_1 and B_2, may be taken as a typical example If the mixed solution is passed through a column of a strong acid exchanger the bases will be quantitatively adsorbed in the form of their cations. If the adsorption affinity of the resin for the two cations differs sufficiently a large scale separation by the break-through method might be feasible This is only likely, however, if the two cations differ in valency In such a case the exchange equilibrium, say

$$\begin{aligned} &2\,RSO_3^- \quad B_1H^+ + B_2H_2^{2+} \\ &= (RSO_3^-)_2 \quad B_1H_2^{2+} + 2\,B_1H^+ \end{aligned} \qquad (7)$$

would lie far to the right hand side, and the B_1H^+ cations at first adsorbed on the resin would be effectively displaced by the $B_2H_2^{2+}$ from later additions of solution The process is aided by the fact mentioned earlier, that a multivalent ion is relatively more strongly adsorbed at low concentrations , as a result of this the $B_2H_2^{2+}$ advancing down the column will maintain a sharp front

Usually both bases will be monacidic, and probably an elution procedure will be used Occasionally the two bases might be separated by a judicious choice of mixed solvents, or by a chemical reaction in the solution phase which preferentially removed one base or the other from combination with the resin , but the most general method of separation will be by the process of displacement development, described earlier, using a stronger base than either as the developer The developer pushes the other bases before it down the column, where they are continually re-adsorbed by salt formation At each stage preferential adsorption occurs, until finally the separation is complete The bases should then emerge from the column in separate zones, the weakest base first, and each transition from one zone to the next should be marked by an abrupt change in pH value and in conductivity

The mechanism of the development may be visualized by considering a mixed band where the two bases B_1 and B_2 are adsorbed in the proportions x/y As the developer advances, some of the bases will be released from the resin in these proportions, but if B_1 is the stronger base its degree of ionization will be greater in the resulting solution, and

$$[B_1H^+]/[B_2H^+] > x/y \qquad (8)$$

Equilibrium with the mixed band however requires that

$$[B_1H^+]/[B_2H^+] = k\ x/y \qquad (9)$$

where k will be close to unity if the adsorption is primarily an electrostatic process into which strong specific adsorption affinities do not enter The movement towards equilibrium will therefore cause B_1H^+ from the solution to exchange with B_2H^+ at the resin surface, and the solution passing on will be enriched in the weaker base This argument applies whatever may be the size of the ratio x/y, so the separation proceeds to completion and the boundaries between the different zones are self sharpening

In this process of ion displacement development the concentration of the issuing bases is determined by the concentration of the developing solution , the ease of separation, and the pH values of the various zones are determined (assuming k close to unity) by the dissociation constants of the bases The chief disturbing factor to be feared is molecular adsorption of uncharged base This, if it occurs, is a less readily reversible process than ion exchange and will interfere with the sharpness of the separation.

The separation of weak electrolytes can also be carried out on weak exchangers As was pointed out earlier in this article, it will then be advisable to avoid changes in the electrical charge of the resin, and in its degree of swelling, by operating at a constant pH The choice of the optimum pH, which depends on the dissociation constants of the electrolytes to be separated, has been discussed in a recent paper[9]

SEPARATION OF STRONG ELECTROLYTES

Anions or cations can be separated by the same methods, which may be illustrated by the very successful separations worked out for the rare earths[8].

The mixed salt solution is run into a cation exchanger in the hydrogen or ammonium form , the rare earth cations are adsorbed in a narrow band at the top of the column They are then eluted by a solution of ammonium hydrogen citrate adjusted to the optimum pH, and in this way a very high degree of separation is achieved.

The process is again a two stage one, repeated continually down the column The cations are dissolved from the resin as citrate complexes, the differing dissociation constants of which result in a selective solvent action , and the equilibrium between labile complex and simple cation is again disturbed as soon as fresh resin is encountered since the tervalent cations will be very strongly adsorbed in place of the univalent hydrogen or ammonium, a stage at which the selective action of the resin comes into operation The success of the process is partly due to the fact that these two effects reinforce one another The stability of the complex increases with decrease in the radius of the unhydrated cation, but the affinity of the resin for the cation varies in the opposite direction Through both effects, therefore, the smallest cation will migrate down the column with the greatest net velocity, and will appear first in the effluent

The optimum *p*H for a given separation has been determined largely by trial and error Theoretical treatment is handicapped by the complexity of the problem, since a number of complexes are formed *e g* $La(H_2Cit)^{2+}$, $La(H_2Cit)_2^+$, $La(H_2Cit)_3$, $La(HCit)^+$ *etc* If theoretical predictions are attempted it must be remembered that the *p*H and the various concentrations are very different at the surface of the resin from their values in the ambient solution (*cf* the H^+ and Cl^- concentrations given in the example on p 448) This may account for the observation that *Dowex 50* requires a higher measured *p*H than *Amberlite IR 1* , since the former resin has a higher electrical charge density, the actual *p*H at the resin surface may have been the same for both

When the object is the preparation of pure rare earths in considerable quantities, the speed of elution can be greatly increased with only a small sacrifice of selectivity by a slight adjustment of the *p*H from its best value Possibly this is because the differences in the stabilities of the complexes represent a much more important factor in the separation than the selective action of the resin.

SUMMARY

In preparative work, particularly where the affinity of the resin for the two solutes differs very greatly, as when there is a difference of valency, the column may be loaded with solute to the break-through point A multi stage system may then give complete separation on a large scale

More usually, when the separative power of the column must be utilized to the full, a small amount of the mixed ions will first be adsorbed at the top of an exchange column A good separation will then depend on the following :

1 Maintenance of near-equilibrium conditions, ensured by a fine grain size, uniform packing, slow rates of flow, or elevated temperature.

2 A mechanism of selective desorption from the resin For ions of weak electrolytes with markedly differing *K*'s it may be provided by *p*H adjustment For strong electrolytes a conversion to the undissociated form is impossible and must be replaced by complex formation (an alternative possibility for weak electrolytes also)

3 Efficient re-adsorption on fresh resin during transit down the column This may result from a valency difference, or may be brought about on acid or base exchangers by a neutralization reaction It should again be as selective as possible

The relative importance of the processes described under *2* and *3* will vary widely, and either may play the main role in the separation For instance, with amino acid mixtures the separation is mainly governed by differences in *p*K , but where these are very small, as with glycine, alanine and leucine, a separation is still possible depending[9] on differences in adsorption affinity

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Carotenoids and Vitamin A

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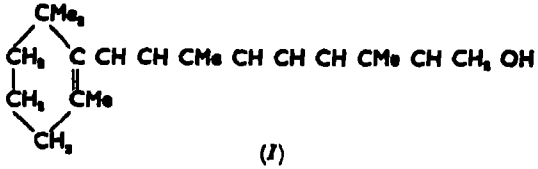
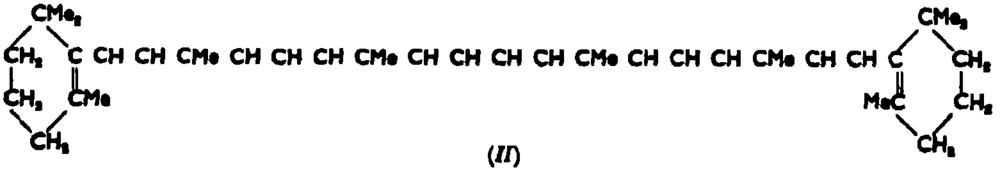
THE importance of vitamin A in human diet is now too well known from the regulations regarding the vitaminization of margarine to require emphasis The physiological activity of the vitamin is characterized by its power to restore growth to animals fed on a diet containing all essentials except vitamin A and by the characteristic degeneration in the structure of the eye known as xerophthalmia which occurs in animals living on a seriously vitamin A deficient diet Manifestation of the latter in humans occurred in an outbreak of this eye disease in Denmark during the 1914–1918 war when poorer people ate little butter and margarine was not vitaminized

The two main sources of vitamin A in human diet are, of course, axerophthol (vitamin A alcohol) *I* and its fatty acid esters, and the polyene colouring matter β-carotene *II* which is responsible for most of the units of vitamin A activity essential to healthy nutrition



(*I*)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(*II*)

The alternative character of carotene and vitamin A in dietaries, which gave rise to some confusion in early investigations when it was observed that the vitamin A activity of certain butters was proportional to the yellow colour mainly attributable to carotene, arises from the conversion of carotene into vitamin A in the animal body This important and remarkably efficient biological conversion is represented in most standard works as a hydrolytic fission of the central double bond in β-carotene with the production of two molecules of vitamin A alcohol, in accordance with the equation

$$C_{40}H_{56} + 2H_2O = 2\,C_{20}H_{29}OH \quad . \qquad (1)$$

This picture seems quite erroneous Apart from the fact that we are unable to recall an example of hydrolytic fission of this type in organic chemical literature, numerous *ad hoc* experiments on the hydrolysis of colloidal solutions of β-carotene with water, aqueous organic solvents in the presence of mild alkali and various emulsifying agents have failed to furnish any evidence of the formation of vitamin A alcohol from such a reaction[1] A number of attempts to accomplish the conversion *in vitro* by means of biochemical agents have also proved unsuccessful Actual chemical conversion of β-carotene into vitamin A alcohol was accomplished in very small yields by oxidative fission to axerophthal (vitamin A aldehyde) and subsequent Pondorff reduction to the alcohol in the year 1942, although this work was not published until 1945[2] From work on rhodopsin[3] it seems likely that these reactions of oxidation and subsequent reduction are also the basis of biological conversion

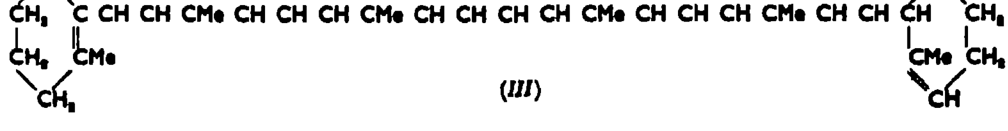
Up to the present the main commercial sources of vitamin A have been whale liver oil and the liver oils of certain fish such as the shark, dogfish, cod, and halibut It was already evident from the increased whaling of the years before 1939 that new sources of vitamin A were necessary and these were subsequently provided to a large extent by high potency shark liver oil The high vitamin A ester content of these arises, presumably, from the cannibalistic nature of the shark towards smaller fish and its function of concentration by storage in the liver As the result of the new commercial demands high potency shark liver oils became scarcer and attention was directed to lower potency oils of the dogfish liver type which presented, however, greater difficulties with regard to deodorization

On the synthetic side, during the 1939–45 war years, much attention was directed to rational synthesis of vitamin A from β-ionone by Sir IAN HEILBRON in this country, O. ISLER in Switzerland, N A MILAS in U S.A., and D A VAN DORP and F J ARENS in Holland At Port Sunlight much research was conducted on the alternative approach of the chemical conversion of carotene into vitamin A. While the yields of vitamin A aldehyde obtained in oxidation experiments on β-carotene are depressingly low, the remarkable efficiency of biological conversion in the rat indicate the feasibility of the project.

With regard to carotene itself, an abundance of this occurs, of course at very low concentration, in the vegetable kingdom and furnishes most of the vitamin A requirements of normal human nutrition. The actual utilization of carotene from vegetables by the body is, however, small. It was early shown by J. C. DRUMMOND and his collaborator[4] at University College, London, that absorption of carotene in rats is dependent on a sufficiency of fat in the diet and that in the absence of this up to ninety per cent was excreted unchanged. It was observed in experiments carried out for the Medical Research Council on human volunteers during 1939–45 that disappearance of carotene from the gastro-intestinal tract was highest when carotene was dissolved in arachis oil or margarine. On average, 28 per cent of carotene given in this form was excreted unchanged, while the percentage excretion from green vegetables was in the region of 60 per cent, and as high as 75 per cent for sliced carrots. It was concluded that a daily dose of 1,300 international units (i.u.) of vitamin A, or of 2,600 i.u. of carotene, was sufficient to cure a mild state of vitamin A deficiency and that the inclusion in the diet of a daily intake of 2,500 i.u. of vitamin A or of 5,000 i.u. of carotene was to be regarded as adequate for the maintenance of adults with a fair margin of safety[5]. Given adequate fat in the diet, the bulk of adult humanity could no doubt obtain its vitamin A requirements from carotene but, apart from individual variation in absorption (which was wide in these human experiments), higher levels are required during pregnancy, maternal nursing, childhood, and illness which can only be attained by dosage with the actual vitamin.

BIOLOGICALLY ACTIVE CAROTENOIDS

Carotene from carrots was found by R. KUHN to contain from 10 to 20 per cent of α-carotene, the optically active isomer *III*, while that from palm oil may contain from 25 per cent to as much as 50 per cent of α-isomer.



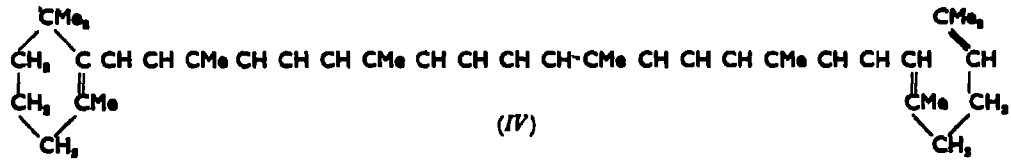
(*III*)

R. KUHN and H. BROCKMANN[6] first observed similar growth responses for α- and β-carotenes in rats fed on a vitamin A free diet but later found that 2.5γ of β-carotene produced the same growth effect as 5γ of α-carotene and concluded that the α-isomer possesses only half the biological activity of β-carotene. A careful biological assay of very pure specimens of α- and β-carotene isolated from *Sherbro* palm oil[7], using Morgan's diet[8] and a large number of animals, has since provided striking confirmation for the 1:2 ratio for the potencies of α- and β-carotene[9].

The 'half activity' of α-carotene and other carotenoids containing a single unsubstituted β-ionone ring is in agreement with the view that conversion of pro-vitamin A active carotenoids to vitamin A occurs by fission of the central double bond of the conjugated system, which is also consistent with the fact that it is the β-ionone ring which is preferentially attacked in the oxidation of α-carotene by alkaline potassium permanganate with production of a biologically inactive apo-α-carotenal[10].

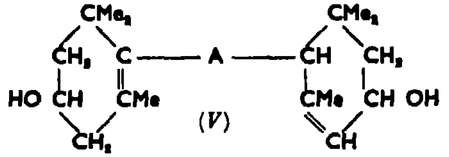
As might be anticipated, the proportion of α- to β-carotene in palm oils varies with the district of origin, the species of fruit, and the earlier history of the oil. It was found that there was little variation in the nature of the carotenoids present in different palm oils, the pale coloured *Malay* oil and the deep red *Busao*[11] representing extremes in which colour and biological activity were largely determined by the carotene present in the form of α- and β-isomers. In a carefully planned investigation, in which a number of samples of oil prepared from specially selected bunches of unripe and ripe palm fruit from a West African plantation was examined, it was found that while the total carotene varied considerably, the proportion of α- to β-carotene obtained from unripe and ripe fruit of the same tree remained constant. The proportion of isomers varied, however, from tree to tree[12].

In addition to α- and β-carotene, R. KUHN and H. BROCKMANN also observed the presence in very small amount of a third isomer *IV* in carotene from carrots, which they isolated by chromatographic technique and named γ-carotene the growth promoting response in rats of which was found to be half of that of β-carotene in accordance with the presence of a single β-ionone ring in the molecule[13]. The presence of γ-carotene in very small amount has also been observed in most of the special palm oils


(*IV*)

examined by the author and his collaborators and it was actually isolated in crystalline condition from a commercial *Sese* palm oil[14]

Substitution of a hydroxyl group for hydrogen in the β-ionone ring of α- or β-carotene results in loss of pro-vitamin A activity The commonest hydroxy derivative is, of course, lutein, which is still frequently called xanthophyll, the name now given to the whole group of biologically inactive oxidized derivatives of the carotenes This pigment which occurs in yellow leaves, egg yolk, and in certain palm oils, is a dihydroxy-α-carotene, formula *V* The corresponding dihydroxy derivative of β-carotene, zeaxanthin, accompanies lutein in egg yolk and is similarly devoid of growth promoting activity while the mono-hydroxy-β-carotene derivative, cryptoxanthin, formula *VI*, which occurs in yellow maize, peaches and also in egg yolk exhibits pro-vitamin A activity in accordance with the presence of the unsubstituted β-ionone ring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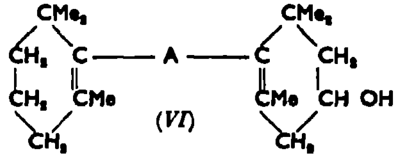

(*VI*)

where A *represents* —CH CH CMe CH CH CH CMe CH CH CH CH CMe CH CH CH CMe CH CH—

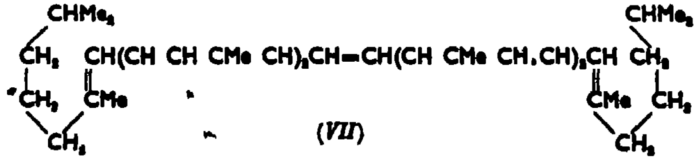
R Kuhn and C Grundmann[15] observed that cryptoxanthin showed growth promoting activity in doses of 5 to 10 γ in contrast to β-carotene which is effective in doses of 2 5 γ More recently it has been reported[16] that the pro-vitamin A activity of all-*trans*-cryptoxanthin is 60 per cent of that of all-*trans*-β-carotene It is interesting to note that an earlier investigation of diets containing α- and β-carotene and cryptoxanthin in the form of fruit and vegetables indicated that cryptoxanthin was of less value than α-carotene as a source of vitamin A for human beings[17]

With regard to the biogenesis of carotenoids, it was early suggested by P Karrer *et alii*[18] that the formation of lycopene in fruits might be pictured as arising from a benzoin condensation of two molecules of phytol aldehyde, followed by dehydrogenation of the intermediate complex

It was later suggested[7] that lycopene, β-carotene, and γ-carotene might be formed simultaneously from such an intermediate complex In such a picture the appearance of γ-carotene in palm oil would correspond to simultaneous operation of both dehydrogenation processes and might account for the very low yields of this isomer isolated from both unripe and ripe fruits In the same paper the formation of α-carotene was pictured as being explainable as arising from asymmetric isomerization of β-carotene by way of a three carbon prototropic change of the type analogous to the racemization of azomethine derivatives observed by C K Ingold and his collaborators[19] On this basis the proportion of α- to β-isomer might be expected to vary with the degree of ripeness of the palm fruit As already mentioned, however, this is not the case and furthermore attempts to effect the interconversion of both β- to α- and α- to β-carotene by heating with *iso*propyl alcoholic sodium *iso*propoxide (compare C K Ingold and C W Shoppee[20]) have proved unsuccessful

EFFECT OF STEREOCHEMICAL CONFIGURATION ON BIOLOGICAL ACTIVITY

As might be anticipated, stereochemical configuration plays an important role in the biological activity of the pro-vitamin A active carotenoids The most active carotenoid is, of course, ordinary crystalline β-carotene, which possesses the all-*trans*-configuration Change of this to the 3-mono *cis* isomer, *neo*-β-carotene U, however, causes a fall to 38 per cent of


(*VII*)

the growth promoting activity of the molecule[31] Change from the all-*trans*-configuration of ordinary α-carotene to the *cis* isomer, *neo*-α-carotene U results in a fall to less than a third of the biological activity of the former (13 per cent of that of all-*trans*-β-carotene[32] A re-investigation of the pro-vitamin A activity of γ-carotene by H J DEUEL and his collaborators[33] has shown, however, that all-*trans*-γ-carotene possesses only 26 per cent, and not half, of the biological activity of all-*trans*-β-carotene and that the *cis* isomer, *neo*-γ-carotene P isolated from ripe berries of *Pyracantha angustifolia* has only 19 per cent of the growth promoting power of all-*trans*-β-carotene[33]

The most characteristic features of the stereoisomerism of the carotenoids are the ease and reversible character of the isomerizations and the small shifts in absorption maxima towards the region of shorter wavelength associated with conversion of *trans* to *cis* linkages Attention was early drawn[34] to the analogy of the mobile *cis-trans* isomerism of carotenoids with azobenzene and it was furthermore observed that β-carotene isomerized more rapidly in toluene (non-polar) than in nitromethane (polar) solution, paralleling G S HARTLEY's observations with regard to azobenzene[35]

CONVERSION OF CAROTENE INTO VITAMIN A

With regard to the conversion of the carotenes and pro-vitamin A active carotenoids into vitamin A in the animal body, it was until recently generally assumed that the liver was the site of conversion The storage of vitamin A in the liver and the fact that there is a decrease in vitamin A formation in the body when this organ is poisoned or damaged lent support to this view It was observed[36], however, that relatively large amounts of carotene may remain in the liver of the rat after its parenteral injection without being utilized although the animal was suffering from vitamin A deficiency Experiments carried out at Liverpool university[37] on goats and other animals indicated that conversion occurs in the intestinal wall R F KRAUS and H B PIERRE[38] have now shown that carotene can be converted into vitamin A in rats in which the liver has been isolated by a ligature on the portal vein It therefore seems probable that the intestinal wall is the main site of conversion in mammals

The early claim of H S OLCOTT and D C MCCANN[39] to have accomplished the conversion of carotene into vitamin A *in vitro* by means of an enzyme obtained from the liver of rats fed on a vitamin A free diet was discredited by the work of J C. DRUMMOND and his collaborator[40]. A later claim[41] with regard to conversion in liver autolysates is unsupported by spectroscopic evidence. Further work carried out by J C. DRUMMOND[42] and his collaborators also furnished negative results

Attempts by R F HUNTER and his collaborator[5] to carry out a purely chemical conversion by oxidation of β-carotene to axerophthal by a variety of reagents proved unsuccessful and a careful repetition of earlier work[6] on the oxidation of β-carotene with alkaline potassium permanganate, which furnished the biologically active β-apo-2- and β-apo-4-carotenals, failed to reveal the presence of any vitamin A aldehyde Finally, the desired reaction was accomplished, but only in very small yield (*c* 1 per cent), by means of hydrogen peroxide in glacial acetic acid, under carefully controlled conditions[5] Hydrogen peroxide suggested itself as a closer approach to biological conditions than other oxidizing agents, and it is interesting to note that the apparent optimum temperature for our experiments (38–40°C) was near to that of the animal body The vitamin A aldehyde which had been previously prepared and characterized[43] was separated by chromatography and reduced to vitamin A alcohol by Pondorff reduction with aluminium *iso*propoxide and the latter further characterized by conversion into anhydro-vitamin A by treatment with alcoholic hydrochloric acid Biological test of a solution of the vitamin thus obtained in arachis oil showed growth promoting activity in rats (ten litter mate growth comparisons) of the order indicated by spectroscopic assay Numerous attempts to improve the yield by variation in the conditions of oxidation proved unsuccessful

This is explicable on the basis of considerations of resonance in extended conjugated systems, since each double bond will lose some of its double bonded character to the neighbouring single bonds, with increase of this effect towards the centre of the system[44] If resonance is indeed responsible for the low yield of vitamin A aldehyde and the *in vivo* conversion does proceed by this reaction, some circumstance must be present which obviates this and permits at least 50 per cent conversion in the rat. This may, of course, be connected with a favoured geometrical configuration of the β-carotene molecule There is much evidence that the effective utilization of carotene in the animal body is intimately connected with the presence of the glycerides of unsaturated fatty acids[45] and it seems not unlikely that the latter, possibly in conjunction with an enzyme, play a significant role in rendering the central double bond prone to oxidation

Before passing to work on the rational synthesis of vitamin A, which comprises the other major subject of this account, reference may be made to recent work on the International Standard for vitamin A

INTERNATIONAL STANDARD FOR VITAMIN A

The isolation of specimens of α- and β-carotene, the physical properties of which indicated that they were purer than any previously described in the literature, led to the request to the author from the Medical Research Council for a preparation to be used as the new ' International ' Standard for vitamin A

The original pure specimen of β-carotene had been prepared from *Sherbro* palm oil but it was decided, for several reasons, to use a grass carotene concentrate as starting material which was known to be free from α-isomer The benefit of much previous experience in chromatography and crystallization obtained in earlier investigations was utilized in this work and spectroscopic examination of the final preparation, at both Port Sunlight[34] and the National Physical Laboratory, indicated that the purity was at least as high as that of the previous International Standard prepared by P KARRER Actually, the melting point of the new preparation was found to be higher

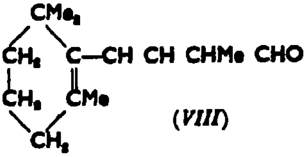
Up to this time the International Standard had been issued from the National Institute for Medical Research as a solution in coconut oil with a nominal potency of 500 i u per gram Examination in late 1945 of a particular sample about which doubt had been expressed showed, however, an E (1 per cent, 1 cm) value of 0 627 at 464 mμ in benzene, indicating a maximal potency of 445 i u per gm and chromatographic analysis of the unsaponifiable matter from this, based on such published information as was available on the biological activity of β-carotene stereoisomers, suggested that the real figure was closer to 350 The actual β-carotene which had been used for the preparation was, however, free from *cis* isomers and gave on chromatography an all-*trans*-β-carotene zone from which 96 5 per cent of the original carotene was recovered At a special conference held with the Department of Biological Standards at the National Institute for Medical Research it was decided to issue the Standard in solution of refined deodorized arachis oil, prepared under conditions ensuring the minimum of isomerization and destruction at a potency of 200 i u. per gm This procedure has now been in use for more than three years and has proved satisfactory.

As a result of the recent report of the sub-committee on Fat-Soluble Vitamins to the expert committee on Biological Standardization of the World Health Organization, however, vitamin A acetate is now being issued as the new standard for vitamin A and the solution of β-carotene in arachis oil has become the International Standard for Provitamin A.

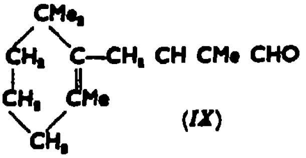
SYNTHESIS OF VITAMIN A AND ALLIED COMPOUNDS

Vitamin A— Whereas perhydrovitamin A was synthesized by P KARRER and his collaborators as long ago as 1933, authentic syntheses of vitamin A have only fairly recently been reported In 1937 R KUHN and C J O R MORRIS[37] described a rational synthesis of vitamin A alcohol from β-ionone, the final stages of which consisted in the condensation of β-ionylideneacetaldehyde with β-methylcrotonaldehyde to vitamin A aldehyde and reduction of this to the alcohol by the Pondorff method, but grave doubt was cast on the validity of this work by the subsequent experiments of P KARRER and A RUEGGER[38] Similarly negative results were obtained in Russia[39] and at the Imperial College[40]

While searching for new routes to vitamin A, the attention of Sir IAN HEILBRON and his collaborators[40] was attracted to a paper by S ISHIKAWA and T. MATSUURA[41] in which the preparation of a C_{14} aldehyde from β-ionone and ethyl chloroacetate was described to which the formula *VIII* was assigned Re-investigation of the reaction[40] showed that the aldehyde actually has the constitution of formula *IX*.



(*VIII*)

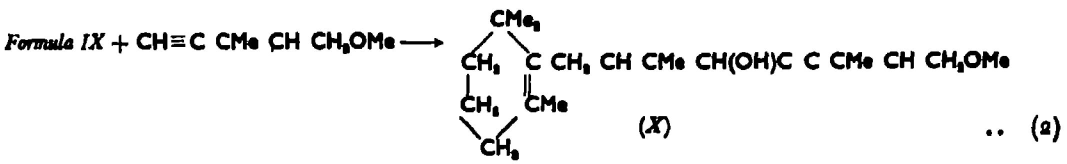


(*IX*)

Combination of this with a ketone molecule

$$Me\ CO\ CH_2\ CH_2OR$$

by way of an acetylene molecule would be expected to lead to a structure convertible into vitamin A Pressure of other work during the war prevented the realization of this in the South Kensington laboratories and the credit of rational synthesis on these lines has to be accorded to O ISLER and his collaborators[42] in Switzerland. In 1946 they described the synthesis of vitamin A methyl ether from the aldehyde, formula *IX*, by condensation with 1-methoxy-3-methylpentenyne, catalytic semi-hydrogenation of the product, formula *X*, and conversion of the hydrogenated product into vitamin A methyl ether by rearrangement and dehydration. The ether, which was first obtained as a yellow oil showing an absorption maximum at 325–328 mμ and



(*X*) .. (2)

reported to possess biological activity 'at least as great as that of β-carotene', has now been obtained in the crystalline form

In the following year O Isler and his collaborators[43] described the successful synthesis of crystalline vitamin A by the route which had been visualized by Sir Ian Heilbron *et alii*[40] The aldehyde *IX* was condensed with the di-Grignard complex of 3-methylpentenynol *XI*, and the resulting glycol *XII* partially dehydrogenated with palladium-charcoal catalyst poisoned with quinoline, and thereafter partially acetylated The resulting monoacetyl derivative *XIII* was then subjected to anionotropic isomerization and simultaneous dehydration by heating with toluene in the presence of a trace of iodine, when vitamin A acetate was obtained The vitamin A alcohol obtained from this was converted into crystalline derivatives from which the crystalline alcohol was obtained by regeneration

$$\text{R}\beta\text{—CH}_2\text{ CH CMe CHO} + \text{CH}\equiv\text{C—CMe}=\text{CH CH}_2\text{OH}$$

(*IX*) (*XI*)

$$\downarrow$$

$$\text{R}\beta\text{—CH}_2\text{ CH CMe CH(OH) C}\equiv\text{C CMe CH CH}_2\text{OH}$$

(*XII*)

$$\downarrow \text{H}_2\text{ partial acetylation}$$

$$\text{R}\beta\text{—CH}_2\text{ CH CMe CH(OH) CH CH CMe CH CH}_2\text{OAc}$$

(*XIII*)

$$\downarrow -\text{H}_2\text{O}$$

$$\text{R}\beta\text{—CH CH CMe CH CH CH CMe CH CH}_2\text{OAc}$$

O Isler and his collaborators[44] have recently reported an improvement on the original synthesis, using phosphorus oxychloride instead of iodine for the final dehydration stage, which gives a 25 to 35 per cent yield of crystalline vitamin A acetate based on β-ionone

Almost simultaneously with the announcement of the synthesis of vitamin A methyl ether by O Isler, alternative syntheses were published[45–47] Methyl-γ-bromocrotonate *XIV* was condensed with β-ionone by the Reformatsky method and the C_{17} acid *XV* was converted into the C_{18} ketone *XVI*[45–47]

$$\text{R}\beta\text{—CH CH COMe} + \text{Br CH}_2\text{ CH CH CO}_2\text{Me}$$

(*XIV*)

$$\downarrow$$

$$\text{R}\beta\text{—CH CH CMe CH CH CH CO}_2\text{H}$$

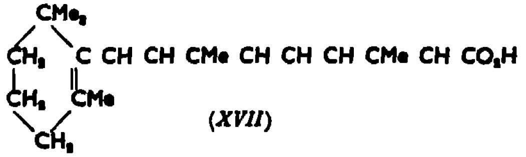
(*XV*)

$$\downarrow$$

$$\text{R}\beta\text{—CH CH CMe CH CH CH COMe}$$

(*XVI*)

D A van Dorp and F J Arens[45] used lithium methyl for the latter stage and Sir Ian Heilbron[47] and his collaborators used cadmium dimethyl The former then condensed the C_{18} ketone with ethyl bromoacetate to give the hydroxy ester, which on dehydration and saponification yielded vitamin A acid *XVII*



(*XVII*)

This acid when dissolved in vegetable oil was found to be only one thirteenth as active as vitamin A, but the sodium salt when buffered to *p*H 10 was found to have biological activity comparable with that of the ordinary vitamin

The C_{18} ketone, for which a new method of synthesis has been described by N A Milas and T M Harrington[48], has been converted into vitamin A aldehyde and thence to the alcohol by the following scheme

(*XVI*)

$$\downarrow$$

$$\text{R}\beta\text{—CH CH.CMe CH CH CH CMe(OH) C}\equiv\text{C OEt}$$

$$\downarrow \text{H}_2\text{/Pd}$$

$$\text{R}\beta\text{—CH CH CMe CH CH CH CMe(OH) CH}=\text{CH OEt}$$

$$\downarrow$$

$$\text{R}\beta\text{—CH CH CMe CH CH CH CMe CH CHO}$$

$$\downarrow$$

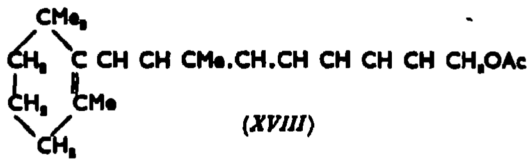
Axerophthol

Norvitamin A— It appears likely from analogy with synthetic work on other biologically active compounds that compounds similar to vitamin A but of simpler constitution may possess biological activity Sir Ian Heilbron and his collaborators[49] are therefore applying the C_{14} aldehyde route to the synthesis of compounds for the study of the relation between chemical constitution and vitamin A activity

Norvitamin A, in the form of its acetate, has been synthesized by condensation of the C_{14} aldehyde with pent-2-en-4-yn-1-ol to give the glycol

$$\text{R}\beta\text{—CH}_2\text{.CH CMe CH(OH)C}\equiv\text{C CH CH CH}_2\text{OH}$$

which on partial hydrogenation, acetylation, and iodine treatment furnished a 25 per cent concentrate of norvitamin A acetate *XVIII*



(*XVIII*)

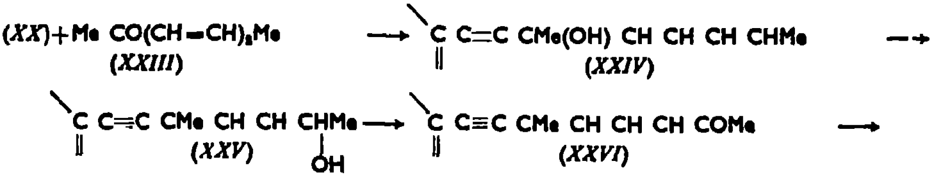
This material was very much less stable than ordinary vitamin A acetate and no accurate biological assay was possible.

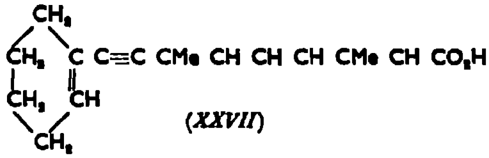
By a similar procedure, the methyl ether of nor-vitamin A, formula *XVIII* with CH_2OMe in place of CH_2OAc, was also synthesized. This material, which was obtained as a 40 per cent concentrate, was also very unstable and showed biological activity to the extent of about 3 per cent of vitamin A itself.

It therefore appears that the presence of the methyl group nearest to the terminal carbinol group of the conjugated chain is essential to both stability and substantial biological activity.

New synthesis of vitamin A and vitamin A analogues—A new route in vitamin A synthesis, which departs from β-ionone as starting material and which promises considerable success, is also being pursued by Sir IAN HEILBRON and collaborators[19]. This commences with the ethenyl*cyclo*hexenes, and the initial interest arose from desire to synthesize demethylated β-ionones for examination of the effect of nuclear methyl groups on the biological activity of vitamin A. Considerable difficulty was encountered in obtaining satisfactory dehydration of ethynyl*cyclo*hexanol *XIX* to give ethynyl*cyclo*hexene *XX* until pyrolysis over aluminium phosphate was investigated. The Grignard complex of ethynyl*cyclo*hexene on condensation with acetic anhydride yielded the acetylenic ketone *XXI*, which on partial hydrogenation gave the required β-ionone analogue *XXII* in poor yield. Neither attempt to obtain an analogue of the C_{14} aldehyde nor condensation with methyl γ-bromocrotonate, however, proved encouraging.

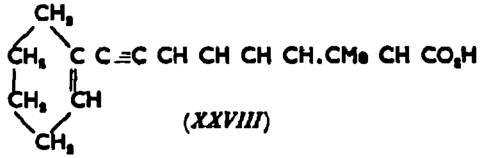
Attention was therefore directed to the alternative approach of condensing ethynyl*cyclo*hexene with the readily available crotonylidene-acetone *XXIII*. The carbinol thus obtained *XXIV* on shaking with acids underwent anionotropic change to *XXV*, which on Oppenauer oxidation gave the ketone *XXVI*. This with ethyl bromoacetate gave the acetylenic vitamin A acid analogue *XXVII* which was isolated in two forms, the sodium salt of one of which showed weak biological activity of the order of 0·1 per cent of that of vitamin A.





(*XXVII*)

In a similar manner, the acid *XXVIII* with a methyl group less in the conjugated chain was synthesized from ethynyl*cyclo*hexene and sorbaldehyde.

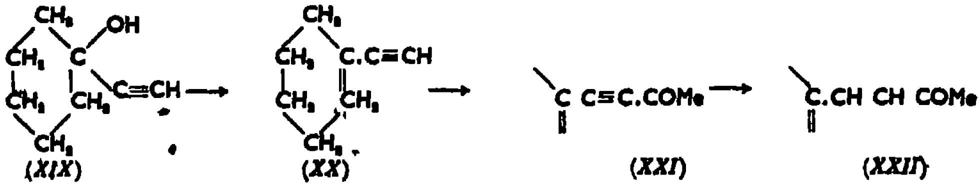


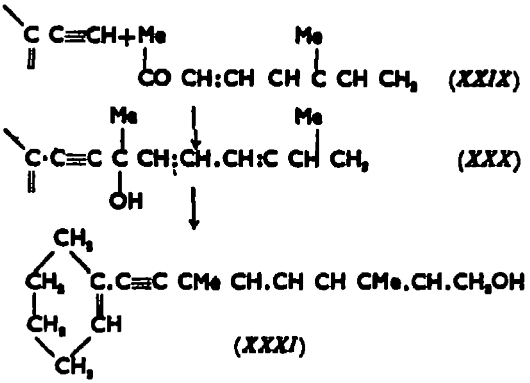
(*XXVIII*)

The sodium salt of this also showed biological activity of the order of 0·1 per cent of that of vitamin A.

Attention has now been directed to the synthesis of the actual analogues of vitamin A alcohol from ethynyl*cyclo*hexene and its methyl derivatives. By condensation of ethynel*cyclo*hexene with vinyl-crotonylideneacetone *XXIX*, the carbinol *XXX* was obtained, which on shaking with acids underwent anionotropic change to the required carbinol *XXXI*.

Vitamin A alcohol also showed biological activity of the order of *c* 0·1 per cent of that of vitamin A.





(*XXIX*)

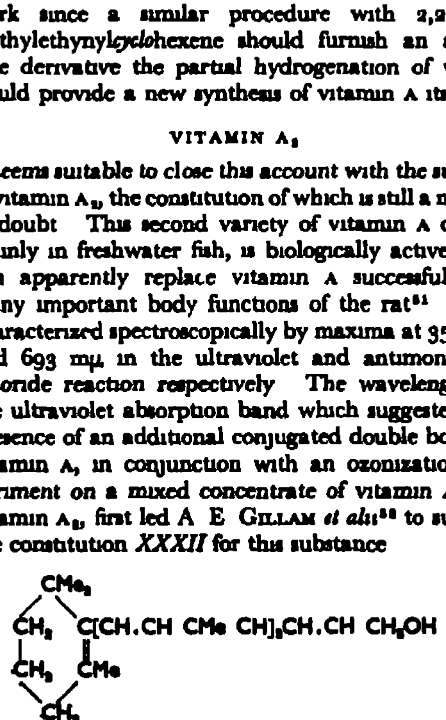
(*XXX*)

(*XXXI*)

Considerable interest is attached to this recent work since a similar procedure with 2,2,6-trimethylethynyl*cyclo*hexene should furnish an acetylene derivative the partial hydrogenation of which would provide a new synthesis of vitamin A itself

VITAMIN A_2

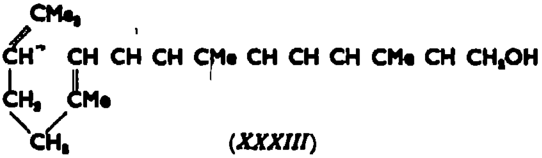
It *seems suitable to close this account with the subject* of vitamin A_2, the constitution of which is still a matter of doubt This second variety of vitamin A occurs mainly in freshwater fish, is biologically active, and can apparently replace vitamin A successfully in many important body functions of the rat[51] It is characterized spectroscopically by maxima at 350 mμ and 693 mμ in the ultraviolet and antimony trichloride reaction respectively The wavelength of the ultraviolet absorption band which suggested the presence of an additional conjugated double bond in vitamin A, in conjunction with an ozonization experiment on a mixed concentrate of vitamin A and vitamin A_2, first led A E GILLAM *et alii*[52] to suggest the constitution *XXXII* for this substance



(*XXXII*)

Following this, R. A MORTON and R H CREED[53] observed that feeding carotene to freshwater fish gave rise to considerably increased stores of both vitamin A and vitamin A_2 in the fish concerned E L. GRAY and J D CAWLEY[54] on the basis of experiments on the 'molecular' distillation of mixtures of vitamin A and vitamin A_2, came to the conclusion that the vitamin A_2 molecule contained the same number of carbon atoms as vitamin A. About this time N D EMBREE[55] also reported the very interesting fact that vitamin A_2, like vitamin A, readily yields an anhydro ('cyclized') derivative on treatment with alcoholic hydrochloric acid which retains the absorption band at 693 mμ in the antimony trichloride reaction, but has ultraviolet absorption maxima identical with those of ordinary anhydro ('cyclized') vitamin A

Following this, P KARRER and his collaborators[56] drew attention to the comparatively small shift of ultraviolet absorption maximum for the supposed additional conjugated double bond in vitamin A_2 and suggested the open-chain formula *XXXIII* for the substance They observed a 65 per cent yield of acetone in degradation of a rich fraction of vitamin A_2 with ozone, which was cited in support of this formula

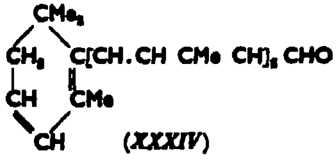


(*XXXIII*)

No evidence was, however, obtained of the formation of vitamin A_2 aldehyde in oxidation of lycopene by hydrogen peroxide under the conditions used for chemical conversion of β-carotene into vitamin A[57]

Further evidence against the original formula *XXXII* is provided by the formation during carotene oxidation by hydrogen peroxide of a higher homologue of vitamin A aldehyde, presumably β-apo-5-carotenal[8], which gave an alcohol furnishing an anhydro derivative with ultraviolet absorption maxima very close indeed (415, 393 and 350 mμ) to those of the product of 'cyclization' of axerophthylidene*iso*propyl alcohol[58]

More recently R A MORTON *et alii*[59] have suggested that vitamin A_2 aldehyde (retinene$_2$) is identical with the C_{20} aldehyde originally obtained by E HAWORTH *et alii*[60] by oxidation of vitamin A alcohol with aluminium *tert*-butoxide in the presence of diethyl ketone for which the formula *XXXIV*, containing an additional conjugated double bond in the β-ionone ring, was suggested



(*XXXIV*)

Difficulty is encountered, however, in the fact that the alcohol obtained from this[59] by the Pondorff method failed to yield anhydro-vitamin A_2 on treatment with alcoholic hydrochloric under the usual conditions. P KARRER[61] has now abandoned the open-chain formula and submitted evidence that vitamin A_2 has the composition $C_{20}H_{28}O$

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Orthoesters of Silicon, Titanium and Zirconium

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ONE of the richest sources of titanium and zirconium is the beach sand of Northern Australia The sands consist chiefly of the minerals rutile, ilmenite and zircon with small amounts of monazite In seeking to utilize these extensive deposits the Australian Council for Scientific and Industrial Research[1] has examined various orthoesters of titanium and discovered promising results from the use of these esters in paints The titanium orthoesters are analogous to the well known silicon orthoesters which serve many useful purposes in industry In this article some account of the fascinating chemistry of the esters of silicon and titanium is given and their utilization in industry is considered In addition some of the recent work on the preparation and properties of zirconium orthoesters is outlined As yet these substances are only of academic interest though it may well be that industrial applications will be found for them

ESTERS OF SILICON

The preparation of silicon tetrachloride by J BERZELIUS[2] in 1824 enabled A EBELMEN[3] in 1846 to produce ethyl and amyl orthosilicates by the following reaction

$$SiCl_4 + 4C_2H_5OH = Si(OC_2H_5)_4 + 4HCl$$

C FRIEDEL and J CRAFTS[4-6], in the course of establishing the tetravalency of silicon, repeated Ebelmen's work and in addition discovered several novel methods for the preparation of mixed alkyl orthosilicates and alkoxy chlorosilanes

$$\begin{aligned} SiCl_4 + 3ROH &= SiCl(OR)_3 + 3HCl \\ SiCl_4 + Si(OR)_4 &= 2Si(OR)_2Cl_2 \\ Si(OR)_4 + CH_3COCl &= Si(OR)_3Cl + CH_3COOR \\ Si(OR)_3Cl + R'OH &= Si(OR)_3(OR') + HCl \end{aligned}$$

In 1885 J HERTHORN[7] isolated the first aryl orthosilicate from phenol and silicon tetrachloride

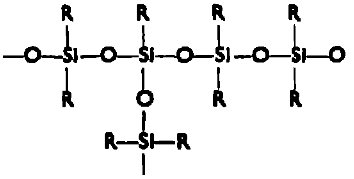
$$4C_6H_5OH + SiCl_4 = Si(OC_6H_5)_4 + 4HCl$$

The yield of alkyl orthosilicate from the reaction of silicon tetrachloride with an alcohol has been steadily improved by the investigations of many workers in this field, notably A DEARING and E REID[8], M KALININ[9] and by H POST and C H HOFRICHTER[10, 11]

A large number of simple and mixed orthoesters have been prepared and examined and their physical properties studied and recorded It is noteworthy that the boiling points of alkyl orthosilicates are not markedly greater than those of the corresponding orthocarbonates

The commercial silicon ester used so widely in this country is an ethyl silicate made from silicon tetrachloride and industrial methylated spirit In addition to tetraethoxysilane (ethyl orthosilicate) $Si(OEt)_4$, it contains esters of polysilicic acids, such as $(EtO)_3Si\text{-}O\text{-}Si(OEt)_3$, since moisture is present in the industrial methylated spirit American ethyl silicates are recorded to be almost pure $Si(OEt)_4$ as they are made from silicon tetrachloride and absolute ethyl alcohol It is also possible to produce silicon esters by the passage of alcohol vapour over heated silicon[12]

Silicones are well known in all laboratories they have the general structure



where R is an alkyl group Depending on the length of the polysiloxane chain $(OSiR_2)_n$ and the amount of cross linking between neighbouring chains, they may be liquids, resins or highly viscous greases possessing heat stable and water resistant qualities In the manufacture of silicones the silicon esters are becoming of increasing importance as intermediates for it is evident that by the hydrolysis of the mono and dialkylated orthosilicates *e g* $R_2Si(OEt)_2$, such complex molecules can arise In 1908 it was established[13] that the silicon esters could react with the Grignard reagent and now the ethoxyalkyl silanes are prepared with great facility by the reaction

$$Si(OEt)_4 + 2RMgI = R_2Si(OEt)_2 + 2Mg(OEt)I$$

Industrially this reaction is utilized in a modified form If the silicon ester, magnesium and an alkyl iodide are brought together under pressure the use of the customary volatile solvent such as ether can be dispensed with In this way commercially useful intermediates like $RSi(OEt)_3$ and $R_2Si(OEt)_2$ may be made

Developments are foreshadowed in the industrial use of silicon esters derived from complex alcohols These can be made by an interchange reaction between the appropriate alcohol and a lower alkyl orthosilicate. To bring about such a reaction, heat and a catalyst are generally required. The completed reaction may be represented as

$$Si(OR)_4 + 4R'OH = 4ROH + Si(OR')_4$$

In the reaction between a lower alkyl orthosilicate and a higher alcohol the replacement is complete only if the lower alcohol is removed as it is formed. If tetraethoxysilane and a higher alcohol are heated together an equilibrium is established between the possible mixed esters and the two alcohols. For example, $Si(OEt)_4$ and ROH will be in equilibrium with $Si(OEt)_3(OR)$, $Si(OEt)_2(OR)_2$, $Si(OEt)(OR)_3$, $Si(OR)_4$ and EtOH. As far back as 1865 Friedel and Crafts[5] showed that two alkyl orthosilicates would interchange alkoxy groups. These investigators reported that from $Si(OMe)_4$ and $Si(OEt)_4$ it was possible to prepare $Si(OMe)_2(OEt)_2$. They claimed in fact that this was the only product. Post and Hofrichter[11] in 1940 reexamined this matter and found that esters with mixed alkoxy groups could be isolated from the reaction mixture in yields required by a statistical redistribution of alkoxy groups. A mixture of ethyl orthosilicate and butyl orthosilicate was heated until equilibrium was attained. Careful fractionation of the product led to the isolation of the following components $Si(OEt)_4$, $Si(OEt)_3(OR)$, $Si(OEt)_2(OR)_2$, $Si(OEt)(OR)_3$ and $Si(OR)_4$ where $R = C_4H_9$. In the hope of preparing substances industrially useful, work has been carried out on the interchange reactions between orthosilicates and polyhydroxy alcohols. For example[14], esters of high molecular weight were products from the reactions of ethyl orthosilicate with glycerol monoacetate. Other examples which have engaged the attention of investigators are, *a* methyl orthosilicate[15] reacting with glucose in the presence of methyl alcohol, *b* lower alkylorthosilicates[14, 16] reacting with ethylene glycol, glycerol and certain carbohydrates respectively. However, this redistribution reaction is not confined to silicon esters and alcohols. The early work of Friedel and Crafts indicated that $SiCl_4$ and $Si(OEt)_4$ would interchange chlorine and ethoxy groups.

In view of the wide interest in fluorine chemistry a result obtained in 1946 by D PEPPARD, W BROWN and W JOHNSON[17] is worth recording. They established that the principal products from the interaction of SbF_3 and SbF_5 with $Si(OEt)_4$ were $SiF(OEt)_3$ and $SiF_2(OEt)_2$. They showed further that the Si-F link remained intact when the alkoxy fluorosilanes underwent alcoholysis. With butyl alcohol the reaction may be represented as

$$Si(OEt)_3F + 3ROH = Si(OR)_3F + 3EtOH$$

unlike the reaction with alkoxy chlorosilanes

$$Si(OEt)_3Cl + ROH = Si(OEt)_3(OR) + HCl$$

At this point it is convenient to consider the hydrolysis of silicon esters as most of their industrial applications involve their behaviour on hydrolysis. Over a century ago Ebelmen[8] studied the reaction of ethyl orthosilicate with water. He concluded that $Si(OEt)_4$ was immiscible with water and reacted slowly to yield alcohol and gelatinous silica. A simple interpretation would be

$$Si(OEt)_4 + 4H_2O \rightarrow Si(OH)_4 + 4EtOH$$

Later work, however, has emphasized that the hydrolysis of an orthosilicate is a complicated process. The hydrolysis reactions are governed by the tendency of silicon compounds with the Si-O-R linkage to condense and form polymers characterized by the Si-O-Si repeating unit. In the simplest case Friedel and Crafts isolated *hexaethoxydisiloxane* $(EtO)_3Si\text{-}O\text{-}Si(OEt)_3$ as one of the products from the reaction of moist alcohol with silicon tetrachloride. The hydrolytic reaction is

$$2Si(OEt)_4 + H_2O = (EtO)_3Si\text{-}O\text{-}Si(OEt)_3 + 2EtOH$$

In 1929 E KONRAD, O BACHLE and R SIGNER[18] prepared various methoxy polysiloxanes by treating methyl orthosilicate with moist methyl alcohol. By careful fractionation of the product which remained after the distillation of unchanged methyl alcohol and methyl orthosilicate, the investigators obtained oils with high boiling points and high molecular weights which proved to be polysiloxanes. About the same time G KING[19] published his well known investigations on the hydrolysis of alkyl orthosilicates in which he emphasized that the setting of silicon ester films depends upon continued hydrolysis which in the limit leads to the formation of a coating of pure silica.

The early attempts to use ethyl orthosilicate as a stone preservative were unsuccessful owing to the formation of a granular silica. However, King discovered that a solution of the orthosilicate in moist alcohol would penetrate the porous surface of decaying stone and then slowly hydrolyse, thus bonding the disintegrating particles of stone with silica. This medium has subsequently been used with great success as a preservative for valuable stonework which had suffered by weathering. Another development was a silicon ester paint suitable for covering stonework, concrete, asbestos *etc*. Various inorganic oxides were incorporated to give special colours. More recently ethyl orthosilicate has been used as a mould binder for precision casting of alloys and also for making synthetic refractories which are porous, acid resisting, hard and thermally stable. The lower alkyl orthosilicates are readily distilled and hence freed from ionic impurities They serve therefore as a convenient source of the very pure silica which is required for making fluorescent powders Certain aryl orthosilicates such as the *o*-cresyl ester are being tested as heat transfer media operating at very high temperatures Research into the preparation and properties of silicon esters is being actively pursued and there is every hope that further uses will be found for these substances

TITANIUM ESTERS

Although silicon and titanium are members of the same family of chemical elements they show marked differences in their own reactions and the reactions of their compounds For example, titanium compounds do not exhibit the degree of complexity characteristic of the silicates It is not unexpected, therefore, that differences are noted in the properties of the respective silicon and titanium esters

It will be recalled that the reaction between silicon tetrachloride and alcohol proceeds to completion in accordance with the following equation

$$SiCl_4 + 4\,EtOH = Si(OEt)_4 + 4\,HCl$$

Titanium tetrachloride, on the other hand, is converted under the same conditions to $Ti(OEt)_2Cl_2\ EtOH$ which is stable even on prolonged boiling with alcohol In fact it has been shown[20] that titanium tetrachloride reacts with methyl, ethyl, *iso*propyl and *iso*butyl alcohols according to the general scheme

$$TiCl_4 + 3\,ROH = Ti(OR)_2Cl_2\ ROH + 2\,HCl$$

Only by further treatment with sodium ethylate NaOEt can the $Ti(OEt)_2Cl_2$ be converted into titanium tetraethylate (ethyl orthotitanate)[20, 21] The methyl orthoester is a solid and the ethyl and other esters are liquids Attempts to find uses for these esters have not been lacking, but it is only recently that promising results have been obtained In the course of some investigations with the object of finding uses for the beach sands found on the north-eastern coast of Australia, various esters of titanium were prepared and butyl orthotitanate appeared to have interesting possibilities in heat resisting paints[1] Paints prepared by simple pigmentation of butyl orthotitanate adhered satisfactorily to glass but on tinplate or steel were powdery and readily removable. However, a paint of exceptional properties was made from aluminium flake, butyl orthotitanate and a glyptal resin Films of a paint of this kind withstood a temperature of 600°C for a prolonged period and large scale trials indicated that as a protective coating for steel under high temperature conditions butyl orthotitanate paints were superior to the conventional heat resisting paints. Experiments showed that when butyl orthotitanate is heated it liberates butyl alcohol slowly Thereby it increases in viscosity until it becomes a thermoplastic solid and finally an insoluble material It is thought that interesting surface coatings might be made from this condensed ester The preparation of the butyl orthoester[1] involves a reaction between butyl alcohol and titanium tetrachloride in the presence of anhydrous ammonia To minimize the formation of viscous products and to ensure a sufficient concentration of ammonia for the chemical reaction, the reaction mixture is cooled to approximately 10°C

$$TiCl_4 + 4\,ROH + 4\,NH_3 = Ti(OR)_4 + 4\,NH_4Cl$$

The chief use for titanium esters appears to be in the production of exceptionally heat resistant paint but other developments, for example as waterproofing agents, are expected to become increasingly important in the near future

ZIRCONIUM ESTERS

The chemistry of zirconium and its compounds is receiving much attention at the present time In particular, interest has focused on zirconium metal which has neutron-absorbing properties and so is included in atomic energy programmes Although zirconium shows important relationships to both silicon and titanium it is distinctive in being capable of a covalency of eight The maximum covalency exhibited by silicon and titanium is six The high covalency of zirconium is reflected in the range and complexity of its compounds

The first mention of the preparation of zirconium orthoesters appears in a communication by H Meerwein and T Bersin[21] in 1929 They treated an alcoholic solution of zirconium tetrachloride with sodium ethylate and after filtering the precipitated sodium chloride found that a crystalline substance separated from the filtrate This substance was recrystallised from xylene and was given the formula $NaH[Zr(OEt)_6]$ The reaction may be written

$$ZrCl_4 + 4\,NaOEt = Zr(OEt)_4 + 4\,NaCl$$
$$Zr(OEt)_4 + NaOEt + EtOH = NaH[Zr(OEt)_6]$$

To obtain the simple orthoester Meerwein and Bersin added the requisite amount of alcoholic hydrogen chloride to the complex salt and obtained the ethyl orthoester $Zr(OEt)_4$ as a solid By using methyl alcohol in these reactions the corresponding methyl derivatives were obtained by the investigators In a later paper Meerwein[22] suggested that the zirconium ester could function as an efficient catalyst for the Meerwein-Ponndorf-Verley reduction of ketones and aldehydes to alcohols

Recently H Funk and E Rogler[24] reinvestigated the reaction between zirconium tetrachloride and phenol and obtained the compounds $Zr(OC_6H_5)_3Cl\ C_6H_5OH$ and $Zr(OC_6H_5)_4\ C_6H_5OH$ as reaction products

We have been engaged in studying the zirconium esters and have obtained a number of interesting results. The esters of certain alcohols have been isolated by treating a solution of zirconium tetrachloride in the alcohol ROH with anhydrous ammonia. By carefully removing the ammonium chloride and excess alcohol the orthoesters were obtained. We have also established that the treatment of a given zirconium orthoester with another alcohol will form a different orthoester by ester interchange.

The reaction between zirconium tetrachloride and ethyl alcohol gives a mixture of two chloroethoxy zirconium derivatives, $Zr(OEt)Cl_3$ EtOH and $Zr(OEt)_2Cl_2$ EtOH

So far the work has been essentially of academic interest but it is highly probable that further research in both the pure and applied fields will yield results of theoretical and practical importance

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The Printing, Packaging and Allied Trades Research Association

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Director of Research

THE Printing, Packaging and Allied Trades Research Association (PATRA) is one of the industrial research associations operating under the aegis of the Department of Scientific and Industrial Research It started (as The Printing Industry Research Association) in a small way in 1931 as an Information Bureau and set up laboratories of its own in 1936 These, in the City of London, were destroyed by fire in an air raid in 1941, and it was not until 1948 that the new laboratories at Leatherhead in Surrey were completed; these occupy some 25,000 sq ft of space devoted to scientific laboratories, printing and packaging workshops, library and offices In 1943 the scope of the Association's work was extended to include work on packaging

In both the Printing and Packaging Divisions the activities of the Association can be grouped under three headings—Information, Advisory Service and Research

INFORMATION

PATRA maintains a comprehensive library covering the technical aspects of printing and packaging and the relevant sciences The information in the form of books, periodicals, pamphlets, reports, catalogues, patent specifications *etc* may be borrowed by members The staff of the library prepare each month two abstract journals—*Printing Abstracts* and *Packaging Abstracts*—covering the fields of printing and packaging respectively. The technical information flowing into the library is card indexed, and from this source reviews of the literature on a wide range of subjects can readily be undertaken.

ADVISORY SERVICE

In addition to receiving help from the library, members consult PATRA on their own individual printing and packaging problems Each year some 1,200 of these inquiries are dealt with, varying in complexity from an item which can be readily answered from existing information to an item which calls for several weeks' laboratory investigation For the latter special inquiry laboratories have been set up—one for printing and one for packaging—so that the day-to-day inquiries shall not curtail the longer-ranged research, although, of course, the research staff are always available to give specialist advice when necessary

PATRA also maintains a package testing laboratory in which packages can be tested for their suitability for transporting goods of various kinds

RESEARCH

The research programme, which includes some twenty six items, is decided by the Research Committee on the advice of the industry given through a Printing Advisory Panel and a Packaging Advisory Panel, and on the advice of the senior scientific staff of the Association An attempt is made to preserve a balance between ' scientific ' items and ' technical ' items, and between short term research which can be expected to give results of practical value in a reasonably short time and long term research which provides the ' background ' information on the underlying principles of the printing and packaging processes and from which the major improvements are most likely to spring

It is obviously not possible in this article to review the whole research programme, but the following brief account of the work of some departments may suffice to illustrate the kind of work which is done in the laboratories

Figure 1. Rotation viscometer

PRINTING INKS

In the letterpress and lithographic printing processes the ink is led from a reservoir to the printing surface by a series of rollers These rollers serve to break down the structure of the ink and distribute it uniformly over the printing surface The efficiency of this operation depends on the distribution system and the characteristics of the ink, and both aspects of this problem are being studied

The construction of the distributing system is such that mathematical estimates of the conditions between the rollers are virtually impossible, and an empirical study of the system is planned using a suitable combination of rollers The apparatus designed for this work is still under construction, but some preliminary experiments made on a standard printing machine to which a specially constructed measuring unit was attached have confirmed the complexity of the problem

To establish the behaviour of printing ink under printing conditions is the aim of fundamental work on the rheology of polyphase systems using a rotation viscometer, *Figure 1* Apart from the efforts of C F GOODEVE[1], and H GREEN[2], little attempt has been made to analyse the results of rheological experiments on printing inks and allied materials in a form which can be of direct help in ink formulation In both these analyses the effect of time has been minimized, in the first instance by using equilibrium conditions, and in the second by operating at constant time Such theories are of limited value when the material is taken from its rest condition and used immediately it has passed through the distribution system, especially when the efficiency of that system is unknown Early work on suspensions of carbon black in mineral oils indicated that Goodeve's theory is not adequate for concentrated suspensions (about ten per cent and over by weight), and the present work involves a detailed study of the effects of rate of shear and time on the condition of the material

Most of the experimental work is done with a concentric cylinder rotation viscometer, but because the capillary tube viscometer is still used by some operators a series of experiments was made to compare the two instruments Dilute suspensions of carbon black in oil were used (five per cent and under), and over comparable rates of shear the agreement between the two methods was satisfactory

An additional result of these experiments was that the suspensions showed anomalous effects even with this low concentration Furthermore, the viscosity/concentration relationship was already more complex than that required by Einstein's equation and required the addition of a quadratic term. With highly concentrated suspensions the viscosity is proportional to a higher power of the concentration

With the rotation instrument more concentrated suspensions are now being used, and a systematic study of the change in consistency with rate of shear, time of shear and of rest has begun

Other work in progress on printing inks is concerned with the drying characteristics In the drying of a printing ink on paper there are two stages—the initial 'setting' of the ink so that the ink will not transfer to another surface under light pressure, and the ultimate hard drying to a rub-proof film It is the initial setting which interests the printer most, since this controls the amount of 'set-off' which occurs A study is being made of the factors controlling the initial setting of inks by regarding the problem as one of filtration—the varnish being filtered out from the ink by the capillarity of the paper Since short intervals of time are involved it is necessary to apply electronic techniques to follow the passage of the varnish into the paper Shorter term problems such as the effect of lithographic damping solutions and the acidity of the paper on the drying rate of inks are also being investigated

THE OPTICS DEPARTMENT

Gloss measurement— A number of uncoated papers have now been examined, ranging from almost complete mat to gloss high enough to give fair mirror images and of luminance factor varying from 25 to 85 per cent These papers have been graded in order by some 180 trade observers and measured on the PATRA-Hilger Goniophotometer[3] The resulting grading is expressed sufficiently well for most practical purposes by the empirical relation

$$G = S(a + 1/L)$$

where G = gloss measured on an arbitrary psychological scale, S = intensity of light specularly reflected at 45°, a = a constant and L = luminance factor of paper

Visual grading of some of the papers depends to a marked extent on the conditions of observation, and with glossy papers the production of clear mirror images is an important factor affecting judgement The surface smoothness and texture of the papers is also taken into account by some of the observers The Sheen glossmeter gives results which are sufficiently close to the visual grading to make this instrument suitable for works control

Opacity— Arrangements have been made with Messrs Evans Electroselenium Ltd for the commercial production of an inexpensive photometer head suitable for routine measurements of opacity of printing papers This embodies (as far as practicable in a simplified apparatus) the recommendations made previously and realized in the Hilger-PATRA Opacimeter[4] The new instrument is less accurate than the standard opacimeter but is sufficiently sensitive and robust for most works purposes

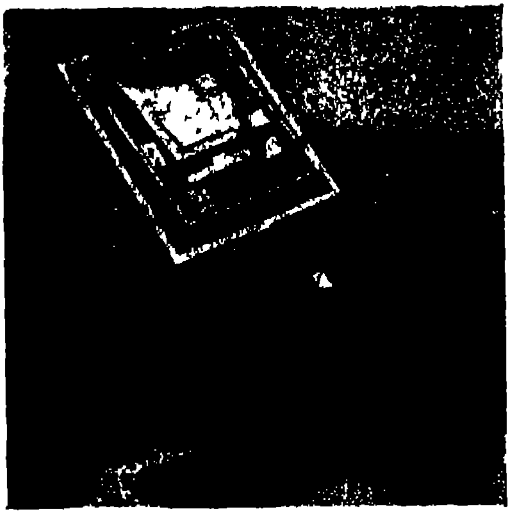

Figure 2 Daylight exposure frame

Colour— A Hilger Uvispek Spectrophotometer is now in operation for the accurate standardization of colours of opaque and transparent materials The light transmitting characteristics of a number of packaging materials have been investigated, and a colour measuring service for the printing and paper industries is being set up

At the instigation of PATRA two forms of 'abridged spectrophotometer' suitable for general works use have been placed on the market One is made by Sheen Instruments Ltd and the other by Evans Electroselenium Ltd Both give approximate spectrophotometric data sufficiently good for works purposes, though not, of course, for absolute standardization

Fading— A daylight exposure frame constructed on an equatorial mounting, *Figure 2*, so as to make the best use of the available sunlight has been installed, and the intensity of the light falling on the samples is automatically recorded by a photocell connected to a recording potentiometer Simultaneous exposures are being made to the light of a carbon arc fugitometer The amount of fading is measured spectrophotometrically, and in this way experimental data are being collected concerning the efficiencies of so-called 'accelerated fading tests'

Tone reproduction— A start has been made in the study of tone reproduction by half-tone photo-mechanical processes. The relative merits of wet and dry plates for process work have been examined and the theory of the formation of the screen image is being investigated

THE APPLICATION OF CONTACT ANGLE DETERMINATIONS TO LITHOGRAPHIC STUDIES

The successful operation of lithography depends on the production and maintenance of surfaces which are either oil wetted (and water repellent) or water wetted (and oil repellent) The printing plate is substantially planographic and is subjected during printing, first to rollers impregnated with an aqueous solution which maintains the non-printing areas in an ink repellent or ' desensitized ' condition, and then to inking rollers charged with an oil-based ink which is accepted by the oil-wettable printing areas and rejected by the desensitized areas

Most normally prepared metal surfaces are readily wetted by oils, and the main problem in lithography is to maintain the non-printing areas in an oil-repellent state To this end the plates used (usually zinc or aluminium) are slightly roughened or grained, and the damping solutions contain small proportions of desensitizing agents such as gum arabic

In order to understand the mechanism of desensitization it is necessary to have a quantitative measure of oil/water wettability, and a contact angle technique has been adopted The apparatus used is basically that described by G MACDOUGALL and C OCKRENT[4] A metal plate 4 × 2 cm is immersed horizontally in the aqueous solution contained in a glass cell At the appropriate moment a drop of oil is released underneath the plate and it rises to the metal surface The profile of the drop is projected on to a screen and the contact angle between the oil/water and the water/metal interfaces is measured Using prepared lithographic surfaces it is found that the printing areas give angles of the order 150° (i e the drop spreads considerably) The non-printing areas give angles approaching 0°—the drop in some cases refusing to form an interface with the metal.

The technique enables a study to be made of many of the variables involved in lithographic printing such as nature of the metal, surface roughness, nature of the oil and its free fatty acid content, and the effect of desensitizers on the production of oil-repellency It should perhaps be emphasized that reproduceable results are only obtained as a result of extreme consistency in preparing the solutions and the metal surfaces Furthermore, since surface corrosion is undoubtedly taking place between the relatively reactive metals used and both the oil and the aqueous phases, conditions are not thermodynamically reversible and the contact angle values may only be used indicatively

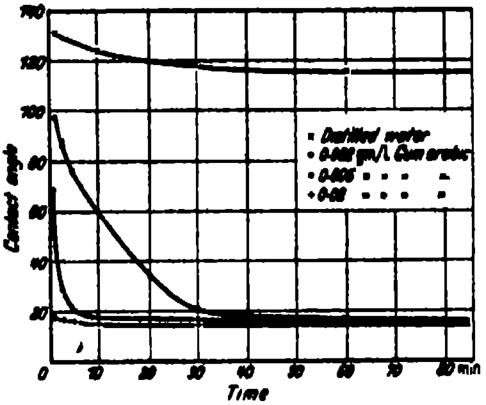

Figure 3 Polished aluminium surface in gum arabic solution

The accompanying graph, *Figure 3*, shows the rate at which a polished aluminium surface becomes desensitized when immersed in a dilute gum arabic solution The time scale refers to the period of immersion of the plate in solution before application of the oil drop Owing to the great dilution at which measurable rates of contact angle change are obtained, diffusion effects must be taken into account when assessing the results, but by experiments of this nature a measure of the effectiveness of a solution as a desensitizer can be obtained Many substances have been investigated and in general those of practical use are all hydrophilic colloids, the effectiveness depending considerably on the presence of certain structures such as the carboxyl group Thus sodium polyacrylate, carboxymethylcellulose, sodium alginate, gum arabic, oxidized starch and methyl cellulose are all very effective Dextrin and polyvinyl alcohol have a slight effect, whilst polyethylene glycol is quite ineffective

BIOLOGY

PATRA is concerned with the attack of books and packages by microfungi and insects, and to this end maintains a biology department

Books may be damaged by moulds in various ways the pages may slowly become stained (foxing), or the binding may suddenly show signs of ' mildew '—as is the case in the tropics and other humid climates—or extensive growth may occur on the binding when new because of incomplete drying after binding or very bad storage conditions

At the beginning of this work, as damaged books arrived at the laboratory isolates of the moulds present were made *Figure 4* gives the frequency of occurrence of the species found *Mycotypha microspora*, Fenner, was found for the first time in Britain, having been reported only once previously in America

The materials used in binding, such as starch paste, animal glue and starch-filled bookcloth, were obviously encouraging growth, as most of the species found were not cellulose destroyers able to grow on paper alone The search for materials which would not provide the necessary food requirements for moulds and insects led to work on synthetic adhesives and bookcloths As it seemed unlikely that synthetic materials would come into use at all rapidly, mould inhibitors had to be found that could be included in the materials in use Many inhibitors were tested, using those species of fungi which had been found most frequently on bindings In the course of this work various morphological effects of the inhibitors on germination were observed A note on the formation of giant cells from the spores of *Aspergillus niger* in the presence of sodium pentachlorphenate has appeared previously in this journal[8]

The same principle of excluding suitable food materials from the binding applies to the control of insect pests, especially where cockroaches, psocids, thysanura and moths are concerned A considerable amount of damage is, however, done by termites and Anobiid beetles of the genera *Catorama* and *Dorcatoma* Tests on the larvae of the Anobiids to determine if they are dependent on materials other than paper are being undertaken at present The problem of termite control has been considered as beyond the scope of this piece of research, as wider issues than bookbinding methods are involved

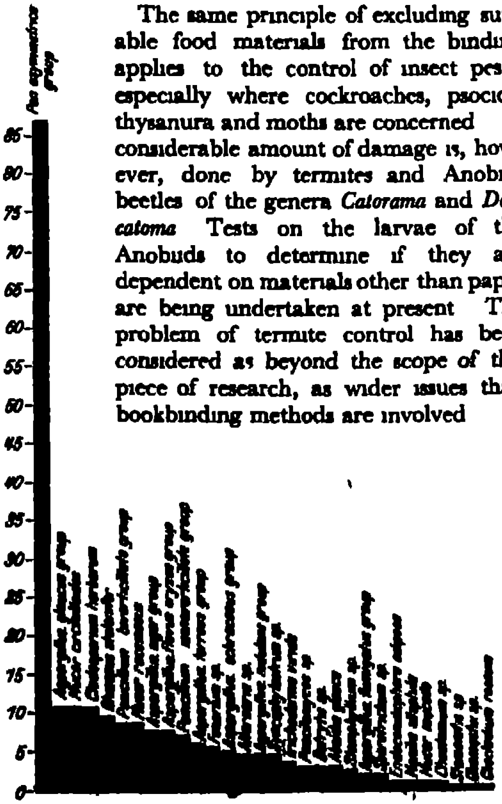

Figure 4 Frequency of occurrence of species

THE RESEARCH OF THE PACKAGING DIVISION

The research work of PATRA's Packaging Division is mainly in the fields of permeability, mechanical strength, and mycology and entomology

The permeability work is concerned with the ingress and egress of gases and liquids which will affect the properties of the packaged goods Typical examples of the industrial application of this work are the prevention of the drying out of tobacco, the corrosion of metal parts and the tainting of foods by extraneous odours, also the prevention of the staining of packages by the penetration of water, oil and grease

In this field the most important aspect is the control of the penetration of water vapour through a package PATRA has developed a standard method[7] for measuring the permeability of barrier materials at normal and tropical conditions down to values of 1 gm per square metre per 24 hours At present a technique for materials of lower permeability is being developed, and this will be applicable to storage conditions used in the quick frozen food industries Work has also been completed on an experimental survey of methods of assessing the 'shelf life' of packed goods This involves a knowledge of the storage conditions, permeability of the package and the permissible change in the relevant property of the commodity

The strength-of-containers research is directed to finding the most efficient manner of packaging to retain the goods satisfactorily and protect them from damage due to mechanical shock in transit and storage Economic considerations are important in the design of packages any increase in packaging costs must normally be offset by the saving in damaged goods due to allowance being made for the increased goodwill where the products are consistently delivered in an undamaged condition It is therefore of little use developing theoretically perfect packages of which the cost is uneconomical

This research is being carried out in three stages

1 the study of normal and accidental transport hazards and the nature and extent of damage experienced under present transport conditions
2 the reproduction of these hazards where possible in the laboratory and a study of the maximum forces to which typical commodities may be subjected without damage
3 a study and correlation of the strength of a container with the mechanical properties of the materials from which it is constructed and the design of the outer case and the internal cushioning.

The first stage of the work is now being conducted as a field survey of road and rail transport conditions The types of hazard include drops, punctures, stacking loads, shunting shocks and vibrations, and vary considerably with such factors as the means of transport, the weight and dimensions of the container and the route

As it is not normally possible to isolate individual factors, statistical methods are being employed in the analysis of the results obtained by personal observation, users' damage reports and trial shipments

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Miscellaneous Notes

NATIONAL RESEARCH COUNCIL, CANADA

RESEARCH equipment, called the Collins Helium Cryostat, has been installed for producing temperatures within a few degrees of absolute zero The low temperature is produced by the liquefaction of helium and is approximately 456 degrees below zero on the Fahrenheit scale, only 4 degrees above absolute zero The new equipment provides a readily available source of very low temperatures for the study of chemical and physical reactions At room temperatures random thermal agitation often masks the subtle effects being investigated, but at these low temperatures thermal agitation is to a great extent eliminated

The binary tube— A special type of vacuum tube has been developed to perform the same mathematical operations that previously required about twenty five conventional vacuum tubes The new tube was invented by J KATZ at the University of Toronto Computing Centre The design was further developed and the first prototype constructed in the tube laboratory of the NRC Division of Radio and Electrical Engineering in Ottawa It is expected that use of the new tube will reduce the cost of the electronic computers in which it is used, and increase their speed and reliability

Division of Applied Biology— Nucleo proteins are the subject of a fundamental study carried out by the biological macromolecules section As research of this type aims at casting light on the chemical basis of inheritance, it must eventually be tied in with the findings of classical genetics *Neurospora* was chosen as the source material because the genetics of this organism have been well worked out and many mutant strains are available

CHEMICAL RESEARCH LABORATORY

A survey of lakes in Libya has recently been undertaken in connection with research into methods of sulphur production These desert lakes are full of micro-organisms known as sulphate reducing bacteria which reduce sulphates to sulphides Sulphur can be produced from hydrogen sulphide by simple aeration The rate of production of sulphide is low and to make the process economically feasible it is necessary to speed up the reduction of sulphates to about ten times its normal rate The research has this object in view

Three methods of research will be used Strains of bacteria from various parts of the world will be examined for their speed of reduction, the influence of different environments will be investigated and methods of obtaining possible quick reducing strains by artificial means will be explored From the results of this work it is possible that an industrial process may be worked out which can be developed on a commercial scale

The sulphate reducing bacteria were originally studied in detail in this country because of their corrosive action on buried pipes It is a good example of the unexpectedness of research that from this apparently unrelated work may spring an industry which will save Great Britain many thousands of dollars and might even, in time, make the country independent of outside supplies

It may be possible to develop an industrial process based on what takes place in the lakes. One small lake contains about half a million gallons and produces about 100 tons of sulphur a year The major part of the research to be carried out must be concentrated on speeding up this process to an economical level, probably about ten times its present rate It might also be possible to exploit natural waters and in this case the time factor would not be so important Sewage is an excellent medium for sulphate reducers and it might be possible to contaminate lakes in desert areas to facilitate large scale production of sulphur This is, of course, a highly speculative idea, but it could be tested easily enough

At present the samples brought back from the desert are being examined and different types of organism isolated When pure cultures of the sulphate reducing bacteria and of the sulphide oxidising organisms are obtained it will be possible to examine their properties and to make experiments on the production of sulphur in various conditions, in different media and to use solid surfaces such as asbestos and coke to see what effect they have on speeding up the process It may also be possible to develop artificially highly active strains of bacteria

CORRECTION

In the last paragraph of the paper ending on p 288 ' nitrogen dioxide ' should be read for ' nitric oxide '

COMING EVENTS

Exhibition of Laboratory Apparatus and Industrial Controllers, Maison de la Chimie, Paris, 18–24 November

International Colloquium on Calculating Machines and Human Thought, Centre National de la Recherche Scientifique, Paris, 8–13 January 1951

New Books

Wild Animals in Captivity

H HEDIGER

Translated from the German by G SIRCOM

(*ix+207 pp, 91 illus, 6 tables, 9½ in by 6 in*)

London Butterworths Scientific Publications, 1950 35s

IN *Wild Animals in Captivity*, Dr H HEDIGER, Director of the Zoological Gardens at Basle, seeks to show that animals in a zoo are better off than those outside—and that they do not lack even freedom. There will be many who will disagree with him, though he does put forward a very strong case—perhaps, he inclined to overstate it—for agreeing that, under the best conditions, captive animals do not suffer unduly The operative clause is, of course, ' under the best conditions ' To accept his thesis we must also forget about the method of capture and transport before being installed in their new homes

Having cleared the ground, even the most sentimentally inclined reader can settle down to enjoy an extensive and reasoned summary of animal behaviour in the wild and in the zoo, beginning with a discussion of territorial needs and social patterns and leading on to relate these to the best treatment under conditions of captivity It is, of course, becoming increasingly apparent that our conception of wild animals being free to wander at will is wholly wrong , they are tied by routine, habit and territorial instinct, to a comparatively restricted space even in the wild The data Dr Hediger has brought together on this point alone make the book worthy of close study, even though its author does too often state the obvious or give complicated explanations of simple facts.

In order to arrive at his conclusions regarding the best methods of confining animals in zoos, Dr Hediger analyses the conditions governing life in the wild, their territorial and sociological requirements, their feeding and breeding problems The effect of his analysis is likely to be twofold , to reassure to some degree those that are over-sensitive or over-sentimental about animals in captivity, and to correct the behaviour, and the attitude, of those who, through ignorance or a natural lack of consideration, are not sensitive enough Apart from the matter concerned purely with animals in captivity, the book is full of interesting details on animal behaviour as a whole There is a serious drawback to the book, however, that quite often the first part of the story is given and the reader is referred to scientific journals (not easily accessible to everybody) for the rest of it , and sometimes the reader is referred to another page for further details, only to find the details are not on that page

M BURTON

A General Kinetic Theory of Liquids

M BORN and H S GREEN

(*vii+98 pp, 10 in by 6¾ in*)

Cambridge University Press, 1949 10s 6d net

ONE of the outstanding achievements in physics since the end of the war has been the publication by Professor BORN and Dr GREEN of a series of papers in which they present a kinetic theory of liquids In the preface to this book they explain that the demand for reprints of these papers was so great that they were unable to meet it Accordingly, they obtained the permission of Council of the Royal Society to republish this group of papers in book form. The book under review consists of five papers on the kinetic theory of liquids and one on the kinetic basis of thermodynamics These are reprinted in the form in which they were originally published over the past four years together with a short appendix of four pages which contains additional notes and corrections

In these papers the authors present a very general outline of a kinetic theory of condensed matter but little is done to apply the ideas which are developed to particular systems Much also remains to be done in developing the theory of quantum liquids, and of the very elementary phenomenon of melting, along these lines This is work for the future, and when it has been completed and the results applied to examine particular condensed systems we shall be in a better position to form a considered judgement of the present contribution At this stage it must be regarded rather as an introduction to a new kinetic approach to the theory of condensed matter—an introduction which has properly aroused the interest and animated discussion of mathematical physicists

The basis of the theory is to define a set of distribution functions corresponding to collisions of any order The equations of continuity are derived and, by introducing the equations of motion, a set of relations is determined from which the distribution functions can be calculated This theory is then applied to examine the general equilibrium and dynamical properties of liquids It is to be noted that these fundamental equations are formulated both in terms of classical and quantum mechanics

The theory of a quantum liquid is developed and it is found that even in equilibrium the 'kinetic' pressure differs from the thermodynamic pressure This leads to a 'duality' of the thermodynamic functions For instance, it is found that flowing helium behaves as though its internal energy were not U but $U - \pi/n$ where π is the difference between the kinetic and thermodynamic pressures and n is the molecular density It is claimed that the main properties of liquid helium II follow from the consideration of thermal processes on this basis It must be remarked that this is an attractive foundation for a theory of liquid helium II, from the consideration that here we have to deal with a *macroscopic quantum* system It has the further advantage that it is not a 'two fluid' theory—a device which always appears to be somewhat artificial

However, the distinction which the authors draw between kinetic and thermodynamic pressure—nay its very existence—has been criticized by Professor DE BOER It is disappointing that the authors did not expand their additional notes sufficiently to include a consideration of these criticisms and their reply to them

A. R. MILLAR

[Interested readers might refer to 'Kinetic Theory of Condensed Matter', a review written by Professor BORN in *Research* 1 (1948) 165 —Ed]

Gmelin's handbuch der Anorganischen Chemie

Eighth edition *Edited by* E H E PIETSCH

No 10 Selenium, Part A2 (*293–414 pp, 105 illus*)

No 28 Calcium, Part A1 (*1–68 pp*)

No 62 Gold, Part A1 (*1–100 pp, all 10 in by 7 in*)

Clausthal-Zellerfeld Gmelin Verlag G m b H, 1950

DM 28 00, 15 50 and 22 50 respectively

VOLUME No 10 of Gmelin covers in detail the whole field of the electrical and photoelectrical properties of selenium The section on electrical properties is short (7 pp) and the remainder of the book is devoted to the photoelectric effect in selenium The factors which influence this are dealt with systematically and a very complete bibliography is given which includes the patent literature on the subject There is also a full account of the technical aspects of selenium photocell production and operation It can safely be said that so complete a review of the subject has not hitherto been published and the book should be of the utmost value both to academic workers and to those in industry who make and use photoelectric cells of this type

These volumes Nos 28 and 62 represent the first to appear dealing with calcium and gold, and both are devoted to a historical review of the chemistry of the elements and their compounds The staff of the Gmelin Institute includes experts in this particular field and they have done their work well Interest in the history of chemistry is not particularly wide, but the many users of Gmelin have at least the consolation that additional volumes on these elements may be expected to appear shortly There are indeed most encouraging signs that work on the Handbook is now progressing rapidly, and that the present edition will be completed before many years

H J EMELÉUS

Technique of Organic Chemistry, Vol II

Catalytic, Photochemical and Electrolytic Reactions

Edited by A WEISSBERGER

(*ix+219 pp, illus, 9 in by 6 in*)

New York Interscience Publishers, Inc, 1949 $5 00

London Interscience Publishers, Ltd, 1949 40s

THE present work is issued as Volume II of a series, and it is therefore unfortunate that Volume I appeared in two parts, designated respectively as 'Volume I' and 'Volume II'

This book is really three books in one The first section deals with catalytic reactions in batch and flow systems It is strange that so little mention is made of catalytic reduction procedures at atmospheric pressure in batch systems—probably the commonest of all catalytic laboratory processes Considerable attention is given, however, to catalysis in continuous flow systems under various conditions of temperature and pressure, which generally necessitate the use of special equipment not often available in chemical laboratories. The drawings of such special equipment are very well done and of good style, but they are sometimes reproduced on too small a scale for the details to be completely clear

The second section of the book deals with photochemical reactions Because photochemistry has at present little synthetic application, attention is concentrated on the nature of photochemical processes—a topic probably not well known to chemists engaged in synthesis, but which must be appreciated if the use of photochemistry is to be extended successfully in the synthetic field, both facts and presentation are satisfactory Experimental details are given for the photochemical accomplishment of some molecular rearrangements, the production of vitamins D, and of halogenation, although a notable omission is that no reference is made to the photochemical facilitation of brominations using N-bromosuccinimide

The third section of the book is concerned with electrolytic reactions, it gives a brief account of electrochemical principles (with glossary !) and contains a very useful tabular summary of electrolytic reduction processes It should help to popularize a *modus operandi* for the production of organic compounds, which is in general rather neglected in ordinary laboratory practice

C W Shoppee

Introduction to Radiochemistry

G FRIEDLANDER and J. W KENNEDY

(*xiv+412 pp; illus, 8½ in by 5½ in*)

New York John Wiley and Sons Inc, 1949 $5 00

London Chapman and Hall Ltd, 1949 40*s* net

This book is the first publication to deal with radiochemistry, as distinct from that part of the subject dealing with the applications of radioactive tracers, that has appeared since the last edition of the classical text of F A Paneth and G. von Hevesy in 1938.

It is inevitable that such an introduction must devote a substantial section to the physical foundations of the subject; but it is a pleasure to find a description of this material that is so free from the errors that beset the non-mathematical treatment Even such a difficult concept as parity is adequately explained

The instrumentation and practical techniques of the subject are still changing so rapidly that already the emphasis given to various methods of detection and measurement might be modified. For example the use of scintillation methods with photomultiplier tubes is dismissed in half a page and the treatment of Lauritsen type electroscopes is equally summary Nevertheless, the extensive equipment used in modern radioactive measurements and the principles and procedures involved are admirably described

Particularly commendable is the inclusion of an entire chapter dealing with the statistical considerations pertaining to radioactive measurements Of more doubtful value is an appendix (93 pp) devoted to a table of isotopes, very similar to that published by G T Seaborg in the *Review of Modern Physics* in October 1948 The ephemeral character of such tables makes it seem out of place in this book The space occupied might better have been devoted to one or two chapters dealing with radiation chemistry, a topic purposefully omitted from this book, or to extending the last three chapters, which deal directly with radiochemistry

A valuable feature of the book is the collection of exercises, generally of a numerical character, appended to each chapter and forming one of the appendices Well chosen compilations of references are also included It is an interesting reflection on the development and the present state of the subject that these omit mention of the classical handbook of S Meyer and E Schweidler

The book is well produced and suffers from unusually few typographical errors

A G Maddock

Books to Come

Progress in Nuclear Physics I *Edited by* O R FRISCH (*224 pp, 107 illus*) London Butterworth-Springer Ltd 45*s*

Ortskurvengeometrie in der komplexen Zahlenebene W MICHAEL (*c 200 pp, 97 illus*) Basel Verlag Birkhäuser *c S Fr* 20 00

High Polymers, Vol VIII The Testing of Organic Plastics H K NASON New York and London Interscience Publishers Inc

Textbook of Quantitative Inorganic Analysis I M. KOLTHOFF and E B SANDELL London · Macmillan and Co Ltd *c* 30*s*

RESEARCH SUPPLEMENT

Variation of Granularity of a Photographic Deposit with Area of Scanning Spot

R DEBOT, Dr.Sc physiques

The electronic granularity meter previously described facilitates accurate measurement of the variations in the mean square deviations of the transparency σ_T *with the area* a *of the scanning spot A high degree of precision is obtained by taking averages over a large number of individual specimens For negative specimens, the variation differs from one emulsion to another and may also depend on development, it is, however, always quite close to the theoretical law* $\log \overline{\sigma_T}\sqrt{a} =$ *constant For enlarged specimens, the relationship always differs from the theoretical for small scanning spots* $\overline{\log \sigma_T}$ *increases much less rapidly than expected For given conditions of enlargement, a definite relationship between the granularity of a negative and that of its enlargement is being sought*

GRANULARITY OF EMULSIONS

In an earlier article[1] an electronic granularity meter was described Details of its performance have been described elsewhere[2] The present paper reports on a large number of measurements which were made in order to verify the law proposed by SELWYN[3] on theoretical grounds, according to which the mean square deviation of the density multiplied by the square root of the area of the scanning spot is constant for any one granular specimen

It was found[2] that the mean square relative deviations of the transparency as measured by the electronic granularity meter were not to be determined entirely by the specimen and the size of the scanning spot, but depended to an appreciable extent on the chosen scanned line on the specimen, the differences occasionally exceeding 30 per cent At the same time, the measured values were distributed according to the Gaussian law around an average value which can be determined with any required precision by making the number of measurements sufficiently large

The following procedure of measurement was adopted

a Around each point of the granular specimen, 8 circles of radii r_i (i varies from 0 to 7) were scanned such that the circumference of the smallest was 40 to 50 times the diameter φ of the luminous scanning spot, and that the difference between two consecutive circumferences constitutes an appreciable fraction (at least 60 per cent) of φ The mean of these 8 measurements is called $\bar{\sigma}_T$

b By measuring $\log \bar{\sigma}_T$ 2 to 4 times around different points an average value of $\overline{\log\ \bar{\sigma}_T}$ is obtained

In order to test Selwyn's law, one would investigate the change in $\overline{\log \bar{\sigma}_T}$ with the area of the scanning spot This proposition is identical with that originally made by Selwyn except that his densities are replaced by relative transparencies which are nearly proportional to one another[4], and by the use of average values which are essential in order to achieve the accuracy required

The geometrical circumstances of the various measurements are given in *Table I* and the numerical results in *Table II* These were obtained on 17 different types of granular deposits, as follows

1	Panchromatic plate of high sensitivity, density		0 46
2	do		1 50
3	do	different brand	0 86
4	Miniature film		0 43
5	do		1 10
6	do		2 12
7	Cine negative film		0 80
8	Cine positive film		0 11
9	do		0 43
10	do		1 03
11	Process plate		0 60
12	Lantern plate		0 87₁
13	Experimental plate *H3*		0 37
14	do	*H27*	2 43₁
15	do	*H33*	0 74
16	do	*H34*	0 86
17	do	*H35*	0 93

For the commercial emulsions, the conditions of development were those recommended by the manufacturers, for *13* to *15* a normal MQ developer was used, for *16* the same developer was used for a shorter time, and for *17*, a fine grain developer was chosen

Table I

Diaphragm No	φ μ	$\log \sqrt{a}$ μ	r_i (i = 0 to 7) mm
1	4 27	0 578₀	0 03 + 0 0025
2	7 94	0 847₄	0 045 + 0·005
3	11 71	1·016₁	0·06 + 0 01
4	21 58	1 281₆	0 15 + 0 015
5	32 8	1 463₄	0 2 + 0·02
6	42 8	1 580₀	0 3 + 0 03
7	65 0	1 760₄	0·4 + 0·04
8	93 9	1·920₂	0·6 + 0 06

Table II

Specimen No	$\overline{\log \sigma_F\sqrt{a}}$ for diaphragm No								Γ	$\sigma(\Gamma)$
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*		
1	0 241$_9$	0 282$_6$	0 280$_8$	0 265$_6$	0 271$_6$	0 239$_6$	0 282$_4$	0 299$_4$	0 269$_5$	0 021$_8$
2	0 565$_0$	0 551$_8$	0 584$_6$	0 594$_1$	0 601$_6$	0 596$_5$	0 601$_6$	0 618$_6$	0 589$_1$	0 021$_8$
3	0 415$_5$	—	0 448$_6$	—	0 464$_8$	—	—	0 429$_6$	0 439$_6$	0 021$_6$
4	1 966$_5$	1 949$_6$	1 946$_5$	1 925$_4$	1 937$_1$	1 932$_5$	1 930$_6$	1 981$_4$	1 947$_7$	0 020$_7$
5	0 208$_6$	0 196$_5$	0 192$_0$	0 179$_7$	0 180$_9$	0 174$_0$	0 187$_6$	0 215$_4$	0 191$_7$	0 014$_6$
6	—	0 323$_6$	0 330$_8$	0 340$_7$	0 338$_9$	0 322$_6$	0 341$_6$	0 390$_8$	0 341$_3$	0 023$_0$
7	0 117$_9$	0 091$_0$	0 094$_6$	0 084$_3$	0 066$_8$	0 081$_1$	0 105$_0$	0 113$_8$	0 094$_0$	0 016$_5$
8	1 533$_6$	1 536$_5$	1 577$_1$	1 640$_7$	1 702$_6$	—	—	—	—	—
9	1 898$_7$	1 889$_0$	1 904$_1$	1 925$_7$	1 973$_6$	1 976$_6$	0 018$_5$	0 073$_6$	1 954$_0$	0 068$_4$
10	0 139$_7$	0 119$_7$	0 135$_8$	0 139$_6$	0 149$_7$	0 163$_7$	0 158$_9$	0 198$_5$	0 150$_7$	0 025$_7$
11	0 047$_8$	0 061$_1$	0 049$_6$	0 064$_6$	0 054$_6$	0 080$_1$	0 082$_5$	0 084$_6$	0 065$_6$	0 015$_1$
12	0 070$_9$	0 051$_0$	0 032$_8$	0 059$_0$	0 070$_6$	0 093$_8$	0 215$_9$	0 441$_3$	—	—
13	0 291$_7$	—	0 333$_6$	—	0 342$_0$	—	—	0 389$_7$	0 338$_7$	0 040$_2$
14	—	0 627$_4$	—	0 632$_6$	—	0 677$_4$	—	0 686$_5$	0 661$_0$	0 026$_6$
15	0 347$_6$	—	0 384$_6$	—	0 414$_6$	—	—	0 430$_6$	0 394$_0$	0 037$_1$
16	0 356$_6$	—	0 403$_2$	—	0 436$_9$	—	—	0 453$_0$	0 412$_6$	0 041$_6$
17	0 294$_0$	—	0 290$_1$	—	0 266$_8$	—	—	0 247$_7$	0 277$_5$	—

The curves for $\log \sigma_F\sqrt{a}$ as a function of $\log \sqrt{a}$ are shown in *Figure 1*, consecutive experimental points are merely joined by straight lines. These curves and the results in *Table II* reveal that $\overline{\log \sigma_F\sqrt{a}}$ does not vary much from one diaphragm to another, certainly much less than has been reported by earlier workers. The experimental errors are such that one would estimate the dispersion of the values of $\overline{\log \sigma_F\sqrt{a}}$ to be 0 01 for any one diaphragm and specimen. If one adds another 0 01 in order to take into account possible errors in the calibration and construction of the granularity meter, one would assume that any deviation in the value of $\overline{\log \sigma_F\sqrt{a}}$ would not be significant, unless it exceeded 0 02. In *Table II*, Γ is the mean of the values of $\overline{\log \sigma_F\sqrt{a}}$ and $\sigma(\Gamma)$ is their dispersion. In four instances out of 17, $\sigma(\Gamma)$ is smaller than 0 02 (Nos *5, 7, 11, 17*), an examination of the corresponding curves would, however, seem to indicate that the experiments betray a systematic variation of $\overline{\log \sigma_F\sqrt{a}}$ since the points do not lie at random around the average straight line. In particular, for No *11*, the most probable curve would rise slightly and that for No *17* would fall, giving a relationship of the type

$$\log \bar{\sigma}_F + n \log a = \text{constant} \qquad (1)$$

where n would be 0 49 and 0 515 respectively.

For the other 13 specimens, the deviations from the law assumed are greater. For No *12*, one can verify that the rapid growth of $\overline{\log \sigma_F\sqrt{a}}$ with a for larger values of this parameter is caused by another

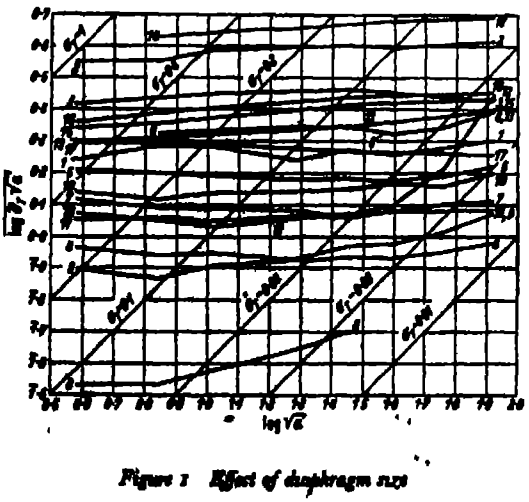

Figure 1 Effect of diaphragm size

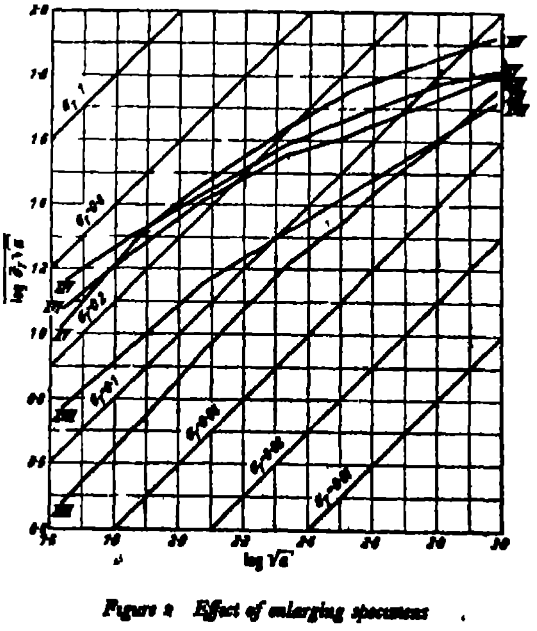

Figure 2 Effect of enlarging specimens

Table III

Diaphragm No	ϕ mm	$\log\sqrt{A}$ μ^2	$\log\sqrt{A/g^2}$ μ^2	R_i (i = 0 to 7) mm
I	0·0487	$1{\cdot}634_9$	$0{\cdot}376_8$	$0{\cdot}3 + 0{\cdot}03\,i$
II	0·0910	$1{\cdot}906_6$	$0{\cdot}648_1$	$0{\cdot}6 + 0{\cdot}06\,i$
III	0·1344	$2{\cdot}074_8$	$0{\cdot}817_3$	$0{\cdot}9 + 0{\cdot}1\,i$
IV	0·2481	$2{\cdot}342_8$	$1{\cdot}083_6$	$1{\cdot}8 + 0{\cdot}2\,i$
V	0·3776	$2{\cdot}524_6$	$1{\cdot}266_9$	$2{\cdot}7 + 0{\cdot}3\,i$
VI	0·5044	$2{\cdot}650_3$	$1{\cdot}391_9$	$3{\cdot}8 + 0{\cdot}4\,i$
VII	0·7483	$2{\cdot}821_8$	$1{\cdot}563_2$	$5{\cdot}4 + 0{\cdot}6\,i$
VIII	1·082	$2{\cdot}981_6$	$1{\cdot}723_4$	$8 + 0{\cdot}8\,i$

factor which does not depend on the granularity, in fact a lack of homogeneity of the emulsion layer. This fact is shown up by a systematic increase in σ_r with the radius of the scanning circle when it becomes greater than 0·3 to 0·4 mm, whatever the size of the scanning spot.

For the other 12 specimens no other foreign phenomenon influences the granularity observations. The largest variations of $\overline{\log\sigma_r\sqrt{a}}$ were observed for a cine positive emulsion (Nos *8*, *9*, *10*) and principally occurred for the lowest densities, for example for a density of 0·43 and over a range of values of a from 44 to 7,000μ^2, $\overline{\log\sigma_r\sqrt{a}}$ grows by approximately 0·2, the antilogarithm of which corresponds to 60 per cent of the minimum value. For the other emulsions the amplitude of the variation is always below ± 7 per cent. If one wants to express some results in terms of equation *1* the values of n will lie between 0·46 and 0·515.

GRANULARITY OF ENLARGED TRANSPARENCIES

Specimens Nos *13* to *17* were enlarged 18·13 times, this factor being denoted by g, and the enlarged specimens by roman numerals. *Table III* gives the conditions under which the results in *Table IV* were obtained, comparable with *Tables I* and *II*. The γ of the enlargement was measured in the granularity meter under the same optical conditions as for the granularity itself.

The mean values of $\overline{\log\Sigma_r\sqrt{A}}$ (the capital letters denote the enlarged specimens) grow rapidly with the area of the scanning spot. Selwyn's law is here not even approximately fulfilled. A comparison of *Figures 1* and *2* proves this strikingly.

Values of $\log\dfrac{\overline{\Sigma_r\sqrt{A}}}{g\gamma}$ were also worked out. Theoretically, if the enlargement of the granularity was perfect, multiplying by the value of γ to take care of changes in contrast, and by g to take care of the increase in linear dimensions, this should be equal to the corresponding value of $\overline{\log\sigma_r\sqrt{a}}$ for the same negative and for a scanning spot of area $a = A/g^2$. It will be seen that in fact the diaphragm VIII, which is the largest used, produced values of $\overline{\log\dfrac{\Sigma_r\sqrt{A}}{g\gamma}}$ which are nearest to the mean of the corresponding negative, the largest differences being of the order of ± 0·04 *i.e.* ± 10 per cent in antilogarithms, and that their arithmetic mean did not differ from zero by more than the experimental error.

Table IV

Specimen No		Diaphragm No								for corresponding negative
		I	II	III	IV	V	VI	VII	VIII	
XIII	$\log\overline{\Sigma_r\sqrt{A}}$	$0{\cdot}478_8$	$0{\cdot}757_1$	$0{\cdot}939_7$	$1{\cdot}217_6$	$1{\cdot}364_4$	$1{\cdot}480_9$	$1{\cdot}610_6$	$1{\cdot}758_8$	—
$\gamma = 1{\cdot}32$	$\log\dfrac{\overline{\Sigma_r}\sqrt{A}}{g\gamma}$	$\bar{1}{\cdot}099_6$	$1{\cdot}378_6$	$1{\cdot}573_7$	$\bar{1}{\cdot}838_6$	$\bar{1}{\cdot}985_4$	$0{\cdot}101_6$	$0{\cdot}231_6$	$0{\cdot}379_9$	$0{\cdot}338_7$
XIV	$\log\overline{\Sigma_r\sqrt{A}}$	$1{\cdot}152_8$	$1{\cdot}333_6$	$1{\cdot}463_4$	$1{\cdot}640_6$	$1{\cdot}746_8$	$1{\cdot}794_1$	$1{\cdot}858_6$	$1{\cdot}919_6$	—
$\gamma = 1{\cdot}09$	$\log\dfrac{\overline{\Sigma_r}\sqrt{A}}{g\gamma}$	$\bar{1}{\cdot}857_6$	$0{\cdot}037_6$	$0{\cdot}169_6$	$0{\cdot}344_6$	$0{\cdot}451_1$	$0{\cdot}498_1$	$0{\cdot}562_7$	$0{\cdot}623_3$	$0{\cdot}881_6$
XV	$\log\overline{\Sigma_r\sqrt{A}}$	$1{\cdot}080_9$	$1{\cdot}330_6$	$1{\cdot}434_4$	$1{\cdot}590_3$	$1{\cdot}669_4$	$1{\cdot}717_3$	$1{\cdot}779_9$	$1{\cdot}812_6$	—
$\gamma = 1{\cdot}46$	$\log\dfrac{\overline{\Sigma_r}\sqrt{A}}{\gamma}$	$\bar{1}{\cdot}580_9$	$\bar{1}{\cdot}908_4$	$0{\cdot}012_9$	$0{\cdot}188_6$	$0{\cdot}247_8$	$0{\cdot}295_1$	$0{\cdot}357_1$	$0{\cdot}390_3$	$0{\cdot}394_6$
XVI	$\log\overline{\Sigma_r\sqrt{A}}$	$1{\cdot}074_6$	$1{\cdot}291_6$	$1{\cdot}413_6$	$1{\cdot}559_3$	$1{\cdot}616_7$	$1{\cdot}667_3$	$1{\cdot}737_6$	$1{\cdot}801_6$	—
$\gamma = 1{\cdot}38$	$\log\dfrac{\overline{\Sigma_r}\sqrt{A}}{g\gamma}$	$1{\cdot}676_1$	$\bar{1}{\cdot}899_3$	$0{\cdot}017_6$	$0{\cdot}160_9$	$0{\cdot}218_4$	$0{\cdot}269_9$	$0{\cdot}339_3$	$0{\cdot}403_3$	$0{\cdot}412_6$
XVII	$\log\overline{\Sigma_r\sqrt{A}}$	$0{\cdot}769$	—	$1{\cdot}157_6$	—	$1{\cdot}431_6$	—	—	$1{\cdot}718_4$	—
$\gamma = 1{\cdot}46$	$\log\dfrac{\overline{\Sigma_r}\sqrt{A}}{g\gamma}$	$\bar{1}{\cdot}346_6$	—	$\bar{1}{\cdot}734_6$	—	$0{\cdot}000_9$	—	—	$0{\cdot}291_6$	$0{\cdot}277_6$

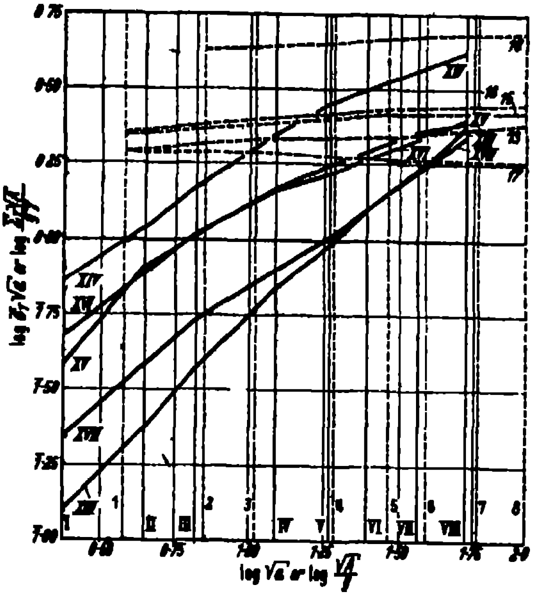

Figure 3 *Effect of scanning spot size on measured granularity*

A more detailed comparison can be carried out in *Figure 3*, which shows the effect of the scanning spot size on the measured granularity both for the negative specimens (dotted) and for their enlargements (smooth) The deviations found as between pairs of curves *i e* the values of

$$\log D = \log \overline{\frac{\Sigma_T\sqrt{A}}{g\gamma}} - \overline{\log \sigma_T\sqrt{a}} \qquad (2)$$

are shown in the hatched portion in *Figure 4* for the specimens *14* to *17* An average curve is also drawn , the maximum deviations from this occur always for the largest scanning spots and go up to ± 0 12 *i e* to ± 30 per cent in antilogarithms They become smaller than ± 0 025 or ± 6 per cent near log $\sqrt{a}$ = 1 5 and increase a little beyond that point

Specimen *13* yielded large values of log *D* for small areas *a* of the scanning spot , these results were plotted separately in *Figure 4* since the enlargement was purposely ill focused, although still within the limits of tolerance of normal enlarging practice

INTERPRETATION AND CONCLUSIONS

The granularity of photographic emulsions can be determined on the electronic granularity meter with good accuracy, of the order of ± 2 per cent in relative and ± 4 per cent in absolute values In order to obtain this accuracy one has to take a mean of a sufficiently large number of individual measurements, as a rule of three groups of eight The values of

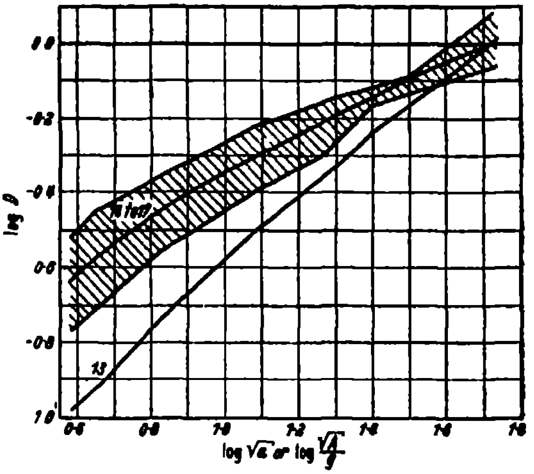

Figure 4 *Deviations from average curve for results of Figure 3*

log $\sigma_T\sqrt{a}$ vary a little with the area of the scanning spot, but the variations observed are smaller than those published by other authors In several instances a law of the type

$$\log \sigma_T + n \log a = \text{constant}$$

is valid, where *n* varies from 0 46 to 0 515, the theoretical law of Selwyn giving a value of *n* = 0 5

Similar measurements can be made on enlarged specimens There is an approximate correspondence between the granularities of a negative and of its enlargement, which is perhaps best seen in the mean curve in *Figure 4* This approximate correspondence applies if the optical conditions of enlargement are always the same and if focusing is done with special care , if not, the experimental deviations become much bigger, the more so if the areas of the corresponding scanning spots *A* and *a* are small It is clear that different optical conditions produce different results, and it is probably premature to attempt to draw definite conclusions

The relationship found between the granularity of a negative and that of its enlargement may be explained if the following conditions are considered

a if the enlargement were optically and photographically perfect, log *D* would be zero ,

b the optical conditions during the enlargement, and in particular the lack of resolution of the lens, produce values of log *D* which are more negative the smaller the scanning spot ,

c from the photographic point of view we must consider that the *γ* of the enlargement is defined for reasonably large areas of the negative or print

The effect of light scatter in the emulsion causes a reduction of the 'microgamma'[5],

on the other hand, for large values of A and a, one might expect positive values of $\log D$ since, apart from measuring the granularity, the scanning of large circles on the enlargement measures the lack of homogeneity of the positive emulsion The mean curve of *Figure 4* effectively appears to cut the line $\log D = 0$ for the last diaphragm used,

the deviations between the mean curve of the variations of $\log D$ with a, and the measured values may perhaps be accounted for to some extent by errors in measuring the granularity and in the optical and photographic conditions of enlargement, principally, in particular for the small diaphragms, by insufficiently exact focusing of the enlarged image

Further experiments will be necessary if the relationship between the granularities of negatives and their enlargements is to be stated more precisely These experiments, and a more detailed discussion as to the reason why earlier authors were unable to obtain granularity values approximately in correspondence with Selwyn's law, will be reserved for a future publication

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Notes on the Deposition of Sands

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In order to establish more information about the conditions of deposition of sands which lead in nature to a loose or dense deposit some of the factors controlling porosity were investigated When it was established that rapid deposition in air and deposition in still water lead to similar and very high porosities with any given sand, and that a slow rate of deposition in air leads to a denser packing than can be achieved by vibration, the velocity of fall of the grains and the intensity of deposition were additionally investigated and their influence on the resulting porosity explained.

THE transport and accumulation of solid particles such as sands and silts by currents of water have received attention from many investigators, but the problems involved are numerous and the results obtained from experimental work are incomplete in many respects One aspect of the wider problem is the question of porosity of sands This has been investigated experimentally by the author[1] and the purpose of the present paper is to describe some of the factors controlling the deposition of sands in water and in air, and to show how these can be expressed in terms of the porosity of the resulting deposit The possible bearing of this work on the interpretation of naturally occurring sediments is briefly indicated

Porosity is a fundamental property of sand The condition of natural aranaceous deposit can be described in terms of porosity in the same way that the state of clay as found in the field can be described in terms of its water content[2] For the latter, the water content of a clay relative to the two limits known as the liquid limit (LL) and plastic limit (PL) is defined by the liquidity index

$$I_L = (\mathrm{LL} - \mathrm{WC})/(\mathrm{LL} - \mathrm{PL}) \qquad (1)$$

where the water content (WC) is defined as the weight of water in the pores of a clay per 100 gm solid material It is measured as a loss in weight after drying to constant weight in a ventilated oven maintained at 105°C The liquid limit is defined as the water content of a clay at which it ceases to behave as a plastic material and becomes essentially a viscous fluid. The plastic limit is defined as the water content at which the clay changes from the plastic to a friable state.

For sands the chief variable which affects porosity is the density of packing of the grains. This is usually expressed as the void ratio e where

$$e = \text{vol. of voids/vol of solids} \qquad (2)$$

It is, however, expressed more fundamentally as the degree of compaction which is defined as

$$(e_L - e)/(e_L - e_D)$$

where e is the void ratio of the sand and e_L and e_D are the void ratios in the loosest and densest possible packings respectively The state of sand in the field can also be described in terms of porosity Porosity P is the percentage of void space that a mass of sand contains i e

$$P = (\text{voids} \times 100)/\text{total volume} \qquad (3)$$

The porosity measured in the field is related to the maximum and minimum porosities at which the sand can exist in stable packing i e

$$\text{Relative porosity } P_r = (P_{max} - P)/(P_{max} - P_{min}) \qquad (4)$$

Maximum porosity is obtained by pouring sand in water without entrapped air The apparatus and procedure have been described[1] Minimum porosity is obtained by vibrating a sand sample under water The apparatus and procedure have been described[1]

Working on the problem of producing experimentally limiting loose and dense packings of sands and studying the variation of P_{max} and P_{min} with different grain shapes, sizes and gradings[1], the author investigated some factors controlling the deposition of sands in water and air It is proposed here to describe these factors, the results obtained will be expressed in terms of porosity

At an early stage of the research it was found that quick pouring of a given weight of sand through air results in higher porosity than can be obtained by slow pouring A series of tests was carried out and the rate of pouring through air investigated It was found that the rate of pouring and the height of drop have a profound influence on porosity It will be seen from *Figure 1*, where typical results obtained for Leighton Buzzard sand 18 to 25 B S S are shown, that the porosity increases with rate of pouring to some limiting value, and this limiting value itself tends to decrease with increasing height of drop These phenomena appeared to be of considerable importance and they were investigated more fully

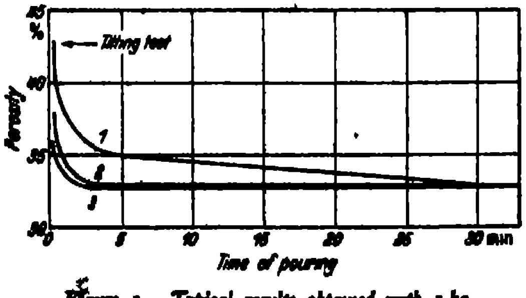

Figure 1 Typical results obtained with 1 kg samples of Leighton Buzzard sands 18 to 25 B S S using a 2 l glass cylinder. Heights of pouring: 1 0 ft, 2 2 ft (0 61 m), 3 6 ft (1 83 m)

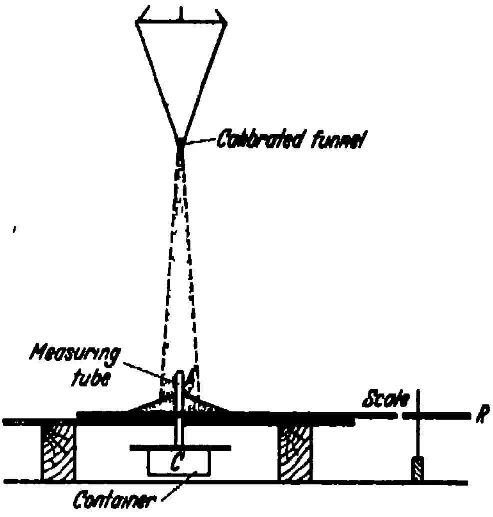

Figure 2 Apparatus for 'stream' deposition on sand surface

GENERAL INVESTIGATION OF FUNDAMENTAL FACTORS CONTROLLING LOOSE PACKING

When pouring sand through water it was observed that after a depth of about 6 in (15 cm) the grains were falling through water in a more or less uniform 'rain' and the porosity obtained was the highest obtained for the sample of each sand used

When pouring sand through air at a high intensity (gm/cm²/sec) the porosity again approached that obtained in water as for example in the tilting test in which a 2 l glass cylinder [3 in (7 6 cm) diam] was used and 1 kg of sand locked inside the cylinder by a rubber stopper was shaken and quickly turned upside down and finally tilted to the initial position and porosity measured, or when the sample was allowed to fall 'instantaneously' in air

It was observed that the porosities obtained by various techniques for producing a rain of grains (perforated funnels and special diffusers were used) tend towards a unique high value with decreasing height of drop On the other hand with the comparatively low intensity of deposition, the porosity of the sand deposited in air was very considerably lower, and also decreased appreciably with height of drop These results were not easily interpreted and, although the actual experimental facts had been reasonably well established, it was clear that, before any logical explanation could be derived, a further investigation was necessary In these latter tests Ham River 25 to 52 B.S S. sand was exclusively employed.

As a first step it was decided to measure the actual intensity of deposition of the sand on the surface of the sample in water and with various techniques of deposition in air In the former where final velocity of fall was noted the average rate of intensity g could easily be calculated by noting the time required to fill the cylinder with 1 kg of sand

The results of these different rates of filling were as follows ·

g = 0 055 gm/cm²/sec
Intensity g = 0 42 „
g = 1 04 „
n = 46 6 per cent
Porosity n = 46 8 „
n = 46 8 „

Each value is the average of at least three tests.

It will be seen that the intensity of deposition had no measurable influence on porosity

In addition, tilting tests were carried out with the cylinder full of water The results of many tests gave the following average values

g = 1 6 gm/cm²/sec n = 47 1 per cent

The porosity is very similar to the values obtained previously

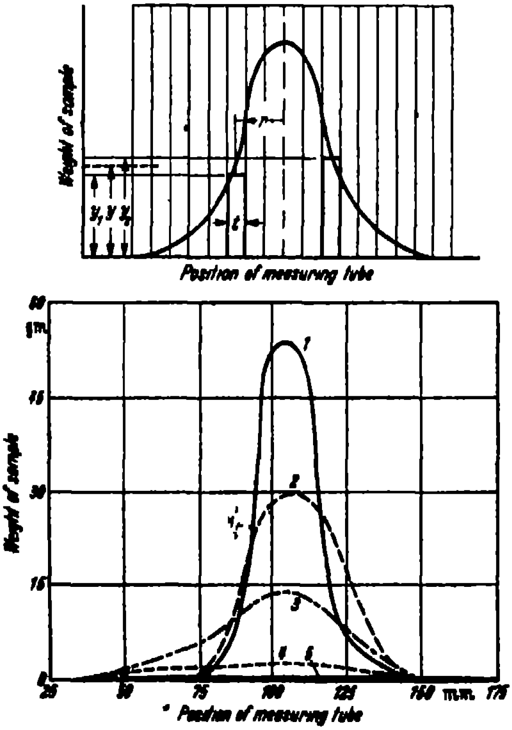

Figure 3 (above) and Figure 4 Cross section tests on sand stream Funnel characteristics D = 0 95 cm, A = 0 237 cm², Q = 4 0 gm/sec, g_f = 17 0 gm/cm²/sec Heights of drop 1 6 in (15 2 cm), 2 1 ft (0 30 m), 3 2 ft (0 61 m), 4 4 ft (1 22 m), 5 6 ft (1 83 m)

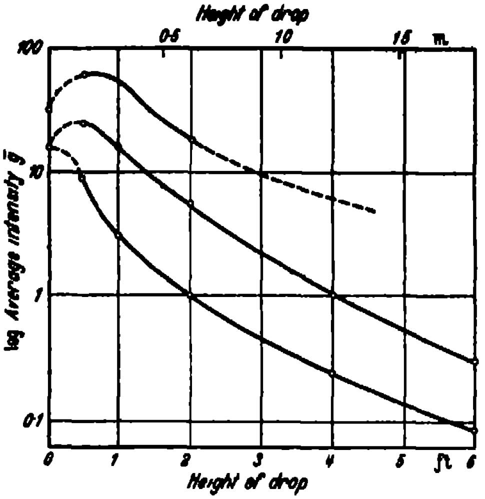

Figure 5 Relationship between log g and height of drop for three different funnels

An attempt was then made to measure the intensity of deposition on the sand surface for deposition in air by the 'stream' of sand The apparatus used is shown in *Figure 2*

A vertical glass tube A with top aperture was moved horizontally by means of the attached wooden scale R and held in each position for a given time The sample of sand collected in the container C was weighed and the weight recorded

Funnels with various rates of discharge were used in the experiments For each funnel and for each height of drop a complete cross section of the stream was investigated, values recorded and plotted as in *Figures 3* and *4* For each of the funnels used the following data were calculated

D = diameter of funnel opening
A = area of funnel opening
Q = discharge of funnel, gm/sec
g_f = Q/A, intensity of funnel
K_1 = $Q/2\pi t\Sigma\eta$, characteristic of measuring tube
g = $K_1\,\Sigma\eta^2/\Sigma\eta$, average intensity

Figure 5 shows the results for three of the funnels used where g is plotted against height of drop.

Finally, in this first stage, the intensities of deposition for various 'rain of grain' techniques were determined These results are given in *Table I*

From *Figure 6* it is seen that the porosities from all the 'stream' and 'rain' techniques appear to plot as a more or less unique function of the intensity That is to say, the very different results obtained with various techniques of deposition can be resolved by using the intensity of deposition as the criterion

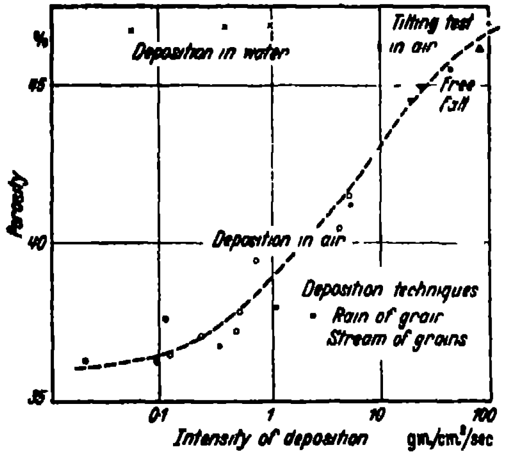

Figure 6 Porosity/intensity of deposition for all tests

Table I

Deposition	*Ht* of drop ft*	*Intensity gm/cm²/sec*	*Porosity*
	0.5	0.76	39.4
	1.0	0.53	37.8
		0.12	37.7
		4.5	40.3
‘*Rain of grain*’ *techniques*	2.0	0.75	36.5
		0.43	37.0
		0.019	36.4
		5.5	41.4
	4.0	0.49	37.2
		0.13	36.4
Free fall (rain)	2.0	85	46.0
Tilting test		120	46.8

* 1 ft = 0.3048 m

This conclusion seemed to be a considerable step forward, but it was at once apparent that the test carried out by depositing the sand under water gave an entirely different result (*Figure 6*)

Consequently, it was necessary to recognize that the intensity of deposition is not the only controlling factor, although it is one of major importance The chief difference between the tests in air and those in water is clearly the great discrepancy between the velocities of fall of grains Following this clue the velocities of fall in water were actually measured and were calculated for air from the following equation

$$v = S_f \sqrt{(2gh)} \tag{5}$$

where S_f is a ‘shape factor’ assumed* to be 0.8 for grains of the sizes used in the present tests. In water $v = 4$ cm/sec while from equation 5 the values calculated for air are given in *Table II*

From these results it is seen that even with extremely small heights of drop the velocities in air far exceed those in water In particular for a 6 in (15 cm) drop, the smallest which had so far been used in the experiments, the velocity in air is 35 times greater than that in water These differences were so large that it was felt they might help to explain the wide discrepancy mentioned above

Table II

*Ht of drop in**	12	6	3	1	0.5
Velocity cm/sec	195	138	97	56	40

* 1 in = 2.54 cm

Consequently, some tests were carried out using a small ‘diffuser’ which delivered a rain of grains over an area of 7 cm², with an intensity $g = 0.14$ gm/cm²/sec This could be regulated to various constant heights above the sand surface The results obtained are set out in *Table III*

Table III

Ht of drop in	0.25 to 0.5	1.5	3	6
Porosity per cent	40.8 41.1 41.2	38.4	37.6	36.8

By plotting porosity n against velocity v the points shown in *Figure 7* were obtained These indicate a definite trend towards the point for deposition in water and in order to provide an intermediate result the sand was deposited in ether—a liquid with a low viscosity In ether the velocity of fall was found to be 12 cm/sec and the intensity was again equal to about 0.14 gm/cm²/sec The porosity was 47.7 per cent which agrees well with the general relationship A tilting test in ether, however, gave a porosity of 46.8 per cent with an intensity of 4.5 gm/cm²/sec

Further decrease in velocity by pouring sand in glycerin (high viscosity) resulted in increased porosity Although the increase of porosity was not as high as could be expected, this could probably be partially explained by the influence of lubrication

DISCUSSION

Before the final explanation was arrived at several hypotheses had been considered These included the possible effect of the stream of sand from the funnels producing a type of ‘digging’ action which increased the porosity above that given by uniform rain The effect of height was considered as being possibly due to an increased compacting action This is, of course, partially true but the correct explanation is the lower intensity of deposition produced by increasing height

However, neither of those effects appeared to explain the high porosities obtained with the tilting test and these results were, almost from the first, explained in terms of some type of ‘locking’ action

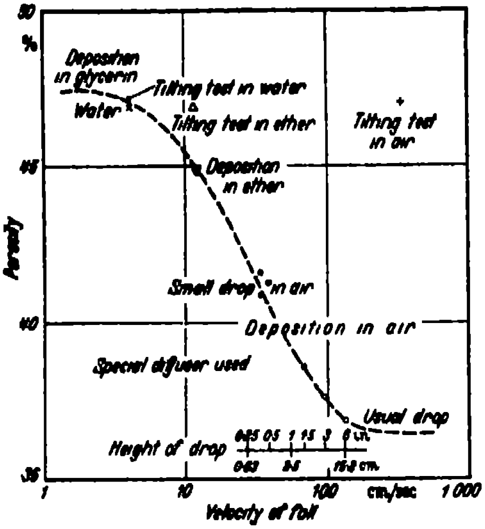

Figure 7 Porosity/velocity of fall relationship for various tests

which prevented a dense packing being obtained Finally the results are explained as follows

1 A low velocity of fall, as for example in water, leads to high porosity, independent of the intensity of deposition

2 A high velocity of fall, as for example from heights of several inches or feet (metres) in air, produces low porosity with low intensity of deposition, but with increasing intensity of deposition the porosity increases progressively until, with a high intensity of deposition corresponding to the free fall of a mass of sand (tilting test), the porosity is of the same order as that obtained by deposition in water

For any given relatively high velocity, the effect of increasing intensity of deposition is to inhibit the possibilities of movement of the grains and they are virtually 'locked' in the open packing existing at any moment in the extreme top layer of the sample To summarize it could be said that with low velocities of fall there is insufficient energy available for producing a dense packing,

With high velocities there is sufficient energy available for a dense packing to be achieved but with high intensities of deposition there is insufficient time available for this close packing to be achieved owing to the 'locking' action of the newly arrived grains

Only when a high velocity is accompanied by a low intensity, which means that the grains behave more or less as individuals, can they be forced into positions of relatively close packing

The movements of sand caused by winds were investigated by BAGNOLD and very detailed experiments were published[8], but in his work the question of density or porosity did not appear to have been considered

In order to obtain data relating to this problem, a wind tunnel was built in which representative samples of wind-deposited sands can be studied In this tunnel some of Bagnold's techniques have been repeated and new ones developed The most suitable methods of measuring porosity were worked out and tested for various wind conditions It is too early to give the full account of the results as the research is not yet complete , but one result already established is of some interest in connection with the contents of the present paper This concerns the relation between average wind velocity and average porosity as shown in *Figure 8* It will be seen that the porosity of sand accumulated by horizontal air currents is greater for lower velocities than for higher This result is in general agreement with those described above i e for sands accumulated by falling vertically through air and water

PRACTICAL APPLICATIONS

The factors described above controlling porosities of sand deposited in air or water seem to be of considerable importance equally to civil engineers and geologists

The latter in studying sediments works in the field and laboratory on the conditions under which the sediments were or are deposited With studies of sands, oolites and other particles the knowledge of relationships between velocity of fall, intensity of deposition and porosity might help to clarify the conditions under which the deposit was or is formed

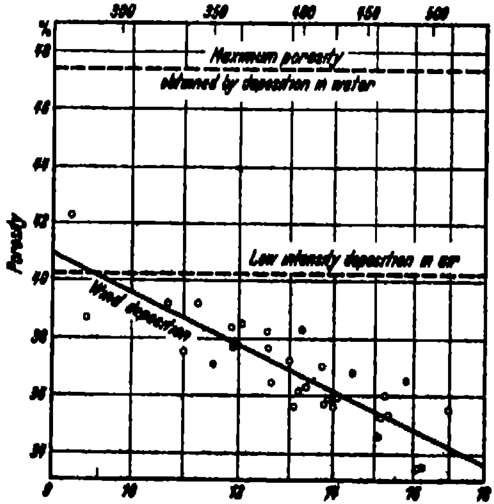

Figure 8 Results obtained with Ham River sand 52 to 100 B.S.S

If the findings included in this paper are conjoined with those indicating the influence of specific gravity, roundness and sphericity of deposited grains on the porosity of the deposited materials, at least the laboratory control of sedimentation should be easier It is known that the investigation of the process of wind deposition of sands as far as the porosity of the deposit is concerned was easier to understand when the problem of vertical deposition was elucidated

In civil engineering, soil mechanics is the subject concerned with the problem described here The possibility of reproducing in the laboratory the porosities of sands found in the field is of great importance Knowing the relation between the rate of pouring and porosity of a given sand, it is now very easy to obtain any required porosity for tests like those run by means of shear boxes or in model footing or pile tests The methods described above which have already been used in soil mechanics' laboratories by other investigators have proved useful

The work described in this paper has been carried out in the course of engineering research in this laboratory The author is greatly indebted to Dr A W Skempton for his encouragement and help, and also wishes to acknowledge the help given to him by A W Bishop during the experimental work Dr F G H Blyth has assisted the author greatly by discussing the contents of this paper with him

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Elastic Thixotropy

Braun, Frey and Reiner[1] refer to experiments with rubber-toluene solutions in which they have found that during continuous shear at a constant speed the viscosity remains unchanged, while the Weissenberg effect rises to a maximum and later drops to zero

Work in these laboratories during the past year on plasticized polyvinyl chloride at about 190°C, tested in a suitably modified version of Weissenberg's[2] rheogoniometer, has shown that the tangential stress component remains nearly constant at constant rate of shear, whereas the normal component rises to a maximum at an applied shear of the order of 100 and then gradually falls to a finite limiting value This behaviour bears an obvious similarity to that of the rubber-toluene solutions, but in addition another aspect of this 'elastic thixotropy' has been observed

Measurements of strain recovery immediately after various amounts of shearing at constant rate have shown that shears up to about 10 are largely elastic, but in this region the original molecular network appears to be finally broken down, and there is a sudden drop in recovery For larger shears the recovery continues to decline and a limiting value is approached at applied shears of the order of 10^4, but at about 10^3 there is an unexplained abrupt temporary increase in the rate of decline On resting at the test temperature the material gradually reverts to its original condition It is noteworthy that, in a plot of recovery against logarithmic applied shear, the two breaks occur at almost the same shear when the rate is increased a hundredfold, and the elastic behaviour in general is even more dependent on the amount of shear than on its rate, though it will be seen that the normal stress component and the recovery reach maximum values at different applied shears The rate of recovery increases with the applied shear, when this exceeds about 10^2, as well as with shear rate These results seem to be consistent with a progressive reduction during shear in the number of secondary cross linkages in the continuously changing molecular network While this would be expected to lower the viscosity, the accompanying reduction in molecular orientation would presumably have the opposite effect

Preliminary experiments with polythene have indicated that this also exhibits 'elastic thixotropy' though the detailed behaviour differs from that of polyvinyl chloride

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1κ, 3κ, 5κ - ('Cis') Cyclohexanetriamine

The crystal structure determination of *α* phloroglucitol dihydrate[1] and diammoniacate[2] show that the hydroxy groups are all in *κ* positions in these compounds and that the water oxygens (ammonia nitrogens) form tetrahedrally distributed hydrogen bonds of medium length It seemed interesting to decide whether the corresponding triamine forms a dihydrate of the same crystal structure

It appears, however, that none of the two possible 1,3,5-cyclohexane triamines have so far been prepared The preparation of the 'cis' form was performed in the following way A solution of 10 gm of 1,3,5-cyclohexane trioxime[3] in 500 cc of absolute ethyl alcohol was reduced by adding rapidly 50 gm of metallic sodium When all sodium had been dissolved the content of the flask was diluted with water and steam distilled The first fraction contained considerable amounts of ammonia Later, a very dilute solution of an alkaline substance distilled The distillation was continued until the distillate was free from alkaline substances The alkaline solution was neutralized with hydrochloric acid and the water evaporated The salt thus obtained was recrystallized from ethyl alcohol containing some water, or in some cases from concentrated hydrochloric acid According to analysis, the composition of the salt corresponds to the formula $C_6H_9(NH_2)_3$ 3HCl H_2O

Calc	C 28 08	H 7 85	N 16 38	Cl 41 47
Found	28 45	7 79	16 00	41 39

The crystals have the shape of hexagonal prisms, but are found to be biaxial and orthorhombic The density observed by Furberg is 1 43 gm/cc, and he found the following lattice constants

$$a = 16\;72\ \text{Å},\quad b = 10\;03\ \text{Å},\quad c = 7\;16\ \text{Å}$$

From these data a 'molecular weight' of 259 ± 4 may be computed, assuming the unit cell to contain four 'molecules' (theoretical mol wt 256 6)

The crystallographic observations seem to make the 'cis' ($\kappa\kappa\kappa \rightleftharpoons \varepsilon\varepsilon\varepsilon$) form of the triamine probable We have, however, prepared a solution of the free base by extracting the solution of the salt in concentrated potassium hydroxide with ethyl ether After adding traces of water to this solution the ether was evaporated in an atmosphere free from carbon dioxide The crystalline mass thus obtained was extremely hygroscopic It was brought into a capillary tube of boron-lithium glass and x-ray powder diagrams were taken, using copper radiation The correspondence between diagrams thus obtained and those of *α* phloroglucitol dihydrate clearly proves the isomorphism of these two substances The crystals therefore contain the triamine in the form of the dihydrate, and with the configuration *κκκ*. As the yield of the synthesis is rather poor we prefer to give further details about the triamine in a later publication

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Low Temperature Ferromagnetism of Sigma Phase in an Alloy Steel

It is known that 18/8/3/1 chromium-nickel-molybdenum-titanium steel heated at and water quenched from 1,150°C consists of austenite, ferrite and a small amount of titanium carbide Recent work[1] has shown that reheating a steel of this structure at 850°C, followed by water quenching, results in the formation of sigma phase

We have now found that sub-zero treatment at various temperatures down to – 196°C of such a steel (Cr, 18 4 per cent, Ni, 8 45 per cent, Mo, 3 40 per cent, Ti, 0 47 per cent, C, 0 04 per cent, Si, 0 56 per cent, Mn, 0 43 per cent), previously heat treated from 0 5 to 100 hours as above to produce sigma, leads to an increase in its ferromagnetism, part of which is permanent and part reversible with change of temperature The permanent increase is caused by the sub-zero transformation of part of the austenite to a ferromagnetic body-centred cubic phase The reversible increase shows that one or both of the normally non-ferromagnetic phases possesses a Curie temperature below which it becomes ferromagnetic

We have separated the austenite and sigma phases from the heat treated steel by means of selective anodic attack in suitable electrolytes, the powder residues obtained being identified by means of x-ray photographs The powders were compacted at 50 ton/in² (80 kg/mm²) and subjected to sub-zero treatment, when only the sigma phase showed a temperature reversible increase in ferromagnetism Thus it is the sigma phase in this steel that possesses the Curie point, it lies at about – 113°C

We hope to publish full accounts of these investigations shortly

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Commentary: Scientific Views of Man

THE EFFECT OF SCIENTIFIC DISCOVERIES on the economic state of mankind has often been discussed, but until recently little attention has been given to the part played by science in forming the 'mental climate' of the time, that is the general idea which people have of their world and of themselves It is beginning to be realized that this influence in Western civilization during the last four hundred years has been very great It is perhaps a sign of this increasing interest in science as a factor determining the general outlook of the times that a book on the origin of modern science should have been written by the Professor of Modern History at Cambridge

Professor H. BUTTERFIELD's thesis is that the scientific movement arose not so much from a closer study of natural phenomena as from the use of a different kind of 'thinking cap' to interpret old and well known observations This 'thinking cap' which proved to be the 'open sesame' to the discovery of the secrets of nature was the attempt to look at things in a more mathematical way, to bring them into abstract and rather geometrical frames of reference which were often considerably remote from anything which could easily be realized on earth Hence it happened and was perhaps inevitable that the laws of motion should spring mainly from the study of the motions of the planets, rather than from actual experiments with terrestrial bodies and projectiles, which owing to the complicating effects of resistance and friction often suggested very different laws For example, terrestrial experiments would seem to show that a constant force was required to maintain a body moving through the air at a constant speed and it required a very considerable effort of the imagination to conceive the idea expressed in Newton's first law, that a body continues to move at a constant speed unless acted on by a force.

If the pioneers of science obtained their successes through using a different kind of 'thinking cap' it is equally true that their discoveries provided men with a new 'thinking cap' with which to study the world and themselves. The first and most devastating result of this was to push Western man off the pedestal he had made for himself in medieval thought. Whatever we may think of medieval life and institutions, they had at least one virtue , they had no doubts about the supreme importance of man. He was a creature only a little less than the angels, created by God in his own image

The lasting and continual effect of scientific discovery during the last four hundred years has been to knock away the supports of this conceit, if we think it such, and to reduce man's stature in his own estimation. Scientists may claim that this is all to the good and results in a saner and truer estimate of man. Many of these repercussions of science on the popular beliefs were however strictly unjustified by the scientific results, which were insufficient to support any opinion on the nature of man, and indeed the popularized view was often not shared by the scientists who knew what had really been discovered and how remote any real knowledge of living things and of human beings was from the simple laws of physics and, at a later stage, chemistry.

THE MECHANISTIC PERIOD

I NEWTON followed up his studies of celestial mechanics with a profound and scientifically unproductive study of the prophecies of DANIEL and it is clear that he was under no delusion of having discovered the nature of man His successors were more confident Impressed by the immense power of mathematics R DESCARTES tried to bring all experience within a mathematical scheme It was the age of mechanics, the science of motion, and of the discovery of primitive machines It was natural for scientists to compare the bodies of animals and of human beings with machines The arms and legs were examples of the principle of the lever, the heart, after the discovery by W HARVEY of the circulation of the blood, could be thought of as a vital pump Starting from this, Descartes said ' the body of man is nothing but a statue or machine made of earth ', a point put more explicitly by G LEIBNITZ in the words ' the body of a man or animal is as mechanical as that which takes place in a watch ' Actually the science of this time was ludicrously inadequate to express any opinion on the nature of the body of man or animals It had not then discovered the nature of the simplest compound Concentrating on certain limited aspects of living things, one could certainly see some analogy with the results of mechanics, the only science which was then known, but how much was left out of the description and how inadequate it was to describe as a machine a self-maintaining, growing, reproducing, sentient organism ! It is true that Descartes admitted in men, but not in animals, the existence of a soul, a ' ghost within the machine ' which gave them free will, feelings and passions

ANIMAL SPIRITS AND ELECTRICITY

At a later period attempts were made to identify the ' animal spirits ' which Descartes had described as ' like a very subtle wind, or rather a very pure and lively flame which, continually mounting in great abundance from the heart to the brain, flows from thence through the nerves into the muscles and gives motion to all the members ' It is natural that attempts should be made to identify it with the electric ' fluid ', developed by electrostatic machines, and when L GALVANI, a professor of physiology and a believer in a ' nervous fluid ', accidentally observed the twitching of frogs' legs when the spinal column was touched by a scalpel, he jumped to the conclusion that he was observing an escape of the electric fluid He concluded that there existed an electricity belonging to animals which was secreted by the brain and resident especially in the nerves ' The principal reservoirs of the electricity are the muscles,' he said, ' each fibre of which may be considered as having two surfaces and possess by that means the two electricities, positive and negative, each of them representing, so to speak, a small Leyden jar, of which the nerves are conductors ' Unfortunately for Galvani's theory, A VOLTA was able, a few years later, to produce electrical effects by the contact of two dissimilar metals, without the intervention of the frog, but Galvani's work continued to interest physiologists who felt that the elusive electric fluid was just the kind of thing they needed J B P LAMARCK was convinced that the nervous fluid ' is electric fluid ' ' Assuredly,' he said ' it can only be a fluid, moving almost with the swiftness of light we have some knowledge of fluids which possess this faculty ' But he thought that it had ' been modified in the animal economy and to some extent animalized by its residence in the blood ' [Quotation from P D WIGHTMAN *Growth of Scientific Ideas*]

THE EVOLUTIONARY DOCTRINE

The critical phase in the conflict between those who regarded man as part of nature and those who claimed that he was outside nature was the evolutionary theory which demonstrated the continuity of human and animal life and C DARWIN's hypothesis which offered a natural law for the development of species and of man from the lower forms of life

The attack on the evolutionary doctrine was made precisely on the ground that it lowered the dignity of man and those who were outraged by the suggestion endeavoured, very unwisely, to oppose the idea by ridicule Bishop S. WILBERFORCE asked in the *Quarterly Review* ' Is it true that all favourable varieties of turnips are tending to become men ? ' and at the discussion held during the British Association meeting at Oxford in 1860, he asked T. H HUXLEY ' I beg to know, was it through his grandfather or his grandmother that he claimed descent from a monkey ? ', a question which brought the crushing retort 'You say that development drives out the Creator , but you assert that God made you and yet you know that you yourself were originally a little piece of matter no bigger than the end of this gold pencil-case. I should feel it no shame to have risen from such an origin, but would be ashamed to be connected with a man who used his great gifts to obscure the truth' Huxley returned to this theme in his Edinburgh lectures *On the relations of man and the lower animals* 'I have endeavoured to show that no absolute structural line of demarcation can be drawn between the animal world and ourselves , and I may add the expression of my belief that the attempt to draw a psychical distinction is equally futile, and that even the highest faculties of feeling and of intellect begin to germinate in lower forms of life At the same time, no one is more strongly convinced than I am of the vastness of the gulf between civilized man and the brutes , or is more certain that whether *from* them or not, he is assuredly not *of* them ! '

One must feel that in this conflict the honours went to the scientist, but all the same, as the popular view filtered down to the masses and as it was interpreted by the politicians, man lost something the survival of the fittest became a political philosophy which justified the use of brute force and helped to undermine the basis of Western civilization—its belief in the supreme value of human beings

RECENT ATTEMPTS OF THE SCIENTIST TO UNDERSTAND MAN

In more recent years the progress of science has on the whole tended to reinforce the common view of man's insignificance and has been used as a basis of what one can only regard as a concerted attack on Western values As late as 1903 A R. WALLACE, one of the pioneers of evolution, in his book, *Man's Place in the Universe*, could claim for the earth and for the solar system a specially favoured and central place in the visible Universe, but recent discoveries have completely dispelled this notion and have revealed a Universe so immense that the mind cannot grasp it This has been used as an argument for the extreme insignificance of the earth and everything on it A Universe of such dimensions could not be designed for anything as insignificant as life—an excellent example of an irrelevant fact being used to justify a personal and probably unjustifiable opinion

It is natural that the increasing knowledge of the chemical structure and working of living material should support a mechanical view of life—now reinterpreted in terms of atoms and molecules Life was a molecular phenomenon 'Life could be regarded as the characteristic stable forms of proteins ' as J NEEDHAM has put it in a recent book J TYNDALL saw that if life was matter, it was necessary to endow the atoms of matter with some of the attributes of life 'Abandoning all disguise,' he said in his famous Belfast address in 1874, ' the confession I feel bound to make before you is that I prolong the vision backward across the boundary of the experimental evidence, and discern in Matter, which we in our ignorance have hitherto covered with opprobrium, the promise and potency of every form and quality of Life.' On this view we shall never find a point at which life, or even thought, begins As we go downwards from ' organisms '—structures undoubtedly living—towards simple molecules, vestiges of life and even perhaps of mind remain —though they can only be recognized as such in the larger assemblages

This is not the place to go into the arguments between materialism and vitalism What I would like to show is that the popular view has often accepted the cruder materialist conclusions and neglected the qualifications with which the more profound scientists hedged them in. The secret of life was always believed to be just round the corner The gap between the living and the non-living was always on the point of being closed When the discovery of the crystalline viruses was made, it seemed that at last the gap between the animate and the inanimate would disappear As one writer said at this time [*Nature, Lond* 145 (1940) 278] 'the further development of such researches may at any moment illuminate the cosmic miracle by which life can only be supposed to have been produced either on this or any other world '.

Further researches however, while they have undoubtedly enlarged our knowledge of life, have still left us completely in the dark as to the mode of formation and nature of these borderline bodies The gap between the living and the non-living, however much it is bridged in some directions, shows an obstinate tendency to reappear in others

The gulf between matter and feeling, between the phenomena which everyone recognizes as the physical basis of perceptions and the perceptions themselves, remains as unbridged as ever To many scientists this gulf is in fact unbridgeable—the perceptions being outside the scientific field altogether M H PIRENNE in his book on *Vision and the Eye*, for example, says ' Physiology as a science does not deny that there are conscious sensations and cognitive reactions it simply does not deal with them ' and ' From its very term of reference physiology deals only with the processes of the organism of which it can study the physical aspects Consequently it can never find anything else—the mind itself will never be seen under the scalpel of the scientists—but it is not entitled to say there is nothing else to be found '

This perhaps goes too far and it may be that at some time in the future a scientific physiological psychology may arise, which discovers in our brain some physical equivalent of our thoughts That the way in which we think and the sensory content of thought depends on the apparatus available seems fairly obvious and it may well be that an increasing knowledge of the apparatus will illuminate the processes of thought, although its inner nature may remain inscrutable But this prospect is still remote , and our profound ignorance and uncertainty as to the real nature of mind might be sufficient to condemn any dogmatic attitude

BIOLOGICAL INTERPRETATIONS OF MAN

Nevertheless the latest scientific discoveries have been avidly seized upon as giving decisive evidence of the nature of man, especially by those who wish to discredit it. The biological attack on the integrity and rationality of man has come from four lines of thought The discoveries of the hormones—substances which have a profound effect on life and personality —led to a popular view that a man's personality was determined by his glands. The fact that mere chemicals can influence behaviour and personality made it seem obvious that living things were nothing but a complex of chemical reactions and personality a chimera

I. P PAVLOV's discovery of the conditioned reflex in animals supported the automatic or reflex nature of animal response to stimuli. Applied to human beings these experiments have been the basis of totalitarian experiments in propaganda and education the object of which has been to make human beings subservient and obedient to a particular political regime S FREUD's investigation of the unconscious motivation of human beings has also done much to undermine the idea of human rationality, since it made it appear that human motives were not within conscious control Freud's ideas had a profound effect on the outlook of the more ' advanced ' people of the period although Freud himself realized their tentative nature

Finally in recent years the mechanical and automatic nature of man has been powerfully reinforced by pressing the analogy between the operations of the brain and those of computing machines—' electronic brains ' as they are called Without wishing to decry the capability and cleverness of these machines and their creators, it is obvious that there are very profound differences between their operations and those of brains The machine is essentially an instrument for counting or comparing impulses of one kind or another It can do this much more rapidly than the human mind is able to It can, for example, add or subtract large numbers in a very short time This is because a sequence of impulses can be added in the time taken by the impulses to pass, which can be made very short In the human brain, on the other hand, counting is a clumsy and troublesome operation We have no way of dealing and adding impulses directly like the machine does We have to turn numbers into words and carry out magical incantations (which we learnt at school) like ' Two and two make four ' —a very different matter to two impulses being added to two impulses to make four impulses which can turn a wheel twice as far as the original two's.

This does not mean that the brain is clumsier and less efficient than the machine because it can do other things which machines so far cannot attempt or only in the most rudimentary fashion. It can recognize the essential pattern of thousands or millions of separate sense impressions. It can produce from this pattern a relevant action—as when the cat pounces on a mouse. It can modify the response to a particular situation by memory of previous experiences *i.e.* it is capable of learning from experience.

Much has been made recently of the fact that a neurone is like some types of electronic valve in its all or none response to a stimulus and a study has been made under the name of cybernetics of the properties of assemblages of units having this property. Even if we admit that this may be a promising approach, the actual results are meagre—a very simple model for the simplest type of memory and a rough mechanical model of how the control of muscles through the senses might be effected. Yet one of the originators of this method, N. WIENER, has described its results, or more exactly its promise, as follows: 'We are beginning to see that such important elements as the neurones—the units of the nervous complex of our bodies—do their work under much the same conditions as vacuum tubes, their relatively small power being provided from outside by the body's circulation, and the book-keeping which is most essential to describe their function is not one of energy. In short, the newer study of automata, whether in the metal or in the flesh, is a branch of communications engineering, and its cardinal ideas are those of the message, of the amount of disturbance or "noise" (a term taken from the telephone engineer), of the quantity of information to be transmitted, of coding technique and so on.' [*Scientific American* 179 (1948) 14]

NEED FOR HUMILITY IN SCIENTIFIC APPROACH

The whole history of science should teach us to be on our guard against seeing in the latest scientific devices a model for the functioning of a living organism. This is not to say that scientists should not make simple models, for much may be learnt from them, but it would be wiser not to make very extensive claims for them. Scientific views of life have been notably ephemeral.

The moral of all this, if one may venture on a moral, would appear to be the desirability of a humble approach on the part of scientists to the problems of nature and life. It may seem out of place to suggest humility at the present moment when scientists can point with pride to fifty years of uninterrupted triumph in almost every department of science. Yet scientists have often been willing to turn a blind eye to regions of experience which are inaccessible to their methods. Their strength has lain in their willingness to do what lies to hand and patiently to work on simpler and hopeful problems without worrying very much about what lies beyond. The fact is that the great advances in dealing with the physicochemical nature of life have not done more than reveal something of the previously unsuspected complexity of the phenomena involved. It is only twenty or thirty years since the important basic substances of living matter began to be isolated by scientific methods and their natures, considered as physical structures, are still largely unknown. A large number of proteins and enzymes have been isolated and purified, but we do not know the structure or mode of action of a single one. Progress has been made in the separation of larger aggregates, such as nucleoproteins, virus bodies and other cell particles, but little is known of their construction and nothing of how they are formed. We know little of the physical basis of reproduction and of the processes which control development and determine the form of complex organisms. The nature of muscular action is still largely unknown and a beginning only has been made in the understanding of conduction in nerves. The working scientists are well aware of the great problems ahead and how little is really known. The picture given by the journalists and popularizers is often very different and scientists owe it to the public to attempt to balance it by stressing what is unknown rather than what has been discovered.

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Spectroscopy at Centimetre Wavelengths

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DURING the war the demand for ever-shorter wavelengths in radiolocation resulted in the reduction of the limit of radio techniques to about one centimetre wavelength This was achieved by the use of new types of oscillator and detector, while the development of waveguide methods of handling radiation served as a reminder of the affinity between radio-waves and optics The latter was further emphasized by atmospheric effects in propagation, scattering by rain drops, and absorption by gases of the atmosphere Theoretical computation of these effects could not be completed without more exact experimental data, and the efforts of physicists were therefore directed into a new region of spectroscopy

In the exploration of this region it was at once obvious that details of the spectrum would be obscured, not by lack of instrumental resolving power, for virtually single-frequency sources were available, but by mutual interactions of the absorbing molecules The energy of the electrical interaction between two molecular dipoles at a distance of 10 Ångström units (Å) is of the same order as the quantum of radiation energy, 2×10^{-16} ergs for 1 cm wavelength Thus in a gas at atmospheric pressure, where the mean distance between molecules is 37 Å, molecular interactions will cause the spectral line to be so broadened that its width is comparable with its frequency Fortunately, in a gas the intermolecular distance can be increased by simply reducing the pressure, and other causes of line-broadening do not become important until pressures of about 10^{-3} mm of mercury are reached In a liquid, on the other hand, the intermolecular distance is much less than 10 Å, and the molecular forces are sufficiently strong to destroy any rotational line spectrum, leaving only the well known Debye relaxation effect In the less viscous liquids, such as water, this produces an enormous absorption at centimetre wavelengths, and the characteristic relaxation time can be determined In the solid, electric dipole effects are very complicated, owing to the huge internal electric field, the latter has no first order interaction, however, with the magnetic moments associated with unpaired electron spins, which exist in paramagnetic and ferromagnetic compounds These spins are relatively free, and precess in an external field of a few kilogauss with a microwave (i e centimetre wave) frequency, application of a perpendicular alternating magnetic field of this frequency will cause the spin to change its orientation in the steady field, with a net absorption of radio-frequency energy This phenomenon, paramagnetic resonance, may also be regarded as the Zeeman spectrum of the ionized atom in the solid state, the transitions being those between the Zeeman components of a single, initially degenerate, atomic level

In the application of microwaves to the study of the three states of matter, the spectra observed in the solid state are thus atomic in nature The same is true also of the remarkable atomic beam experiment of W F LAMB and R C RETHERFORD[1] on the fine structure of the hydrogen atom, which revealed the necessity for a correction to the accepted value of the spin magnetic moment of the electron, associated with its interaction with the electromagnetic field[2] In the liquid and gaseous states, on the other hand, the spectra are those of molecules Interest in the liquid state has somewhat declined, following the initial post-war spurt[3] The gaseous field, however, has attracted a considerable volume of research, particularly in the United States, and its general nature and possibilities are well understood This article will therefore be confined to gases, though the work on paramagnetics, after a later start, is of steadily increasing interest

APPARATUS

Centimetre waves may be regarded as the transition region between radio waves and infra-red radiation The spectra observed belong to the long-wave fringe of the infra-red, but the techniques employed are essentially those of the radio-engineer, with the modifications required by the shortness of the wavelength Radiation is generated by an electronic vacuum tube, usually a klystron, which produces oscillations confined to a band so small that for practical purposes they may be regarded as a single frequency They are detected by a crystal rectifier the action of which is similar to that of the conventional diode, it consists of silicon as a semi-conductor and tungsten as a whisker and is an improved form of the crystal detector familiar to early wireless enthusiasts The radiation is collimated within hollow metallic tubes, waveguides, which prevent spreading of the beam but introduce an attenuation (of the order of 10 per cent power loss per metre of path at 1 cm wavelength) owing to resistive losses on the walls

With these tools the spectroscopist's task would be simple if it were not for the extreme weakness of the spectra to be observed A comparatively strong line, such as the fundamental rotational line of carboxysulphide (OCS), has an absorption coefficient of 5×10^{-5}, that is, the power in a wave traversing the gas would decrease by only 0.5 per cent in a metre distance. Although this is small compared with the resistive losses on the wall of a waveguide, it can of course be differentiated from the latter by observing the change in power transmitted through a length of guide on pumping out the absorbing gas. By using a long length of guide as an absorption cell the absorption due to the gas can be made sufficiently large for measurement. The drawbacks are, however, the great loss of signal power, and interference effects between small reflections in the guide; these change when the gas is removed, owing to its finite refractive index, and obscure the absorption which it is desired to measure. These disadvantages are overcome by using a resonant cavity, consisting of a short length of waveguide closed by conducting walls half a wavelength apart. The radiation is reflected between these walls many thousand times before it decays, and a long effective pathlength is created. Alternatively, one may think of the cavity as a tuned circuit of which the damping or sharpness of tuning is altered by admission of an absorbing gas, and measurement of this alteration provides an accurate method of determining the absorption coefficient of the gas. The method is tedious because the spectral lines must be plotted out point by point as the frequency is changed. It is inconvenient in searching for unknown lines, because the sharply resonant cavity must be continuously tuned to the oscillator.

A quicker method which forms the basis of present-day systems depends on the fact that the absorption due to the gas varies rapidly with frequency as the latter is swept over a narrow spectral line. Thus if the frequency of the oscillator is varied up and down at a low repetition rate (*e.g.* 30 c/s) the signal power transmitted through a waveguide cell containing the gas will dip each time the oscillator frequency passes through an absorption line. The resulting amplitude modulation of the radio frequency signal can be amplified after rectification and the spectral line displayed on an oscillograph screen the time base of which is synchronized with the sweep of the oscillator. *Figure 1* illustrates the principle of this method.

The success of this method arises from its ability to separate the absorption due to the gas (through its sharp change with frequency) from resistive losses on the walls of the guide. Nevertheless its sensitivity is little better than the cavity method, allowing absorption lines of about 10^{-6} per cm *i.e.* 10 per cent power absorption per km, to be detected. The limiting factors are the excessive noise generated by crystal rectifiers at low frequencies, and interference between small reflections in the waveguide cell, which are frequency sensitive because of the long pathlength (paths up to 10 metres have been used). These difficulties are avoided in a novel method of R. H. HUGHES and E. B. WILSON[4], employing the Stark effect. If an electric field of some hundreds of volts/cm is applied to the gas the spectral lines, which are otherwise degenerate with respect to their

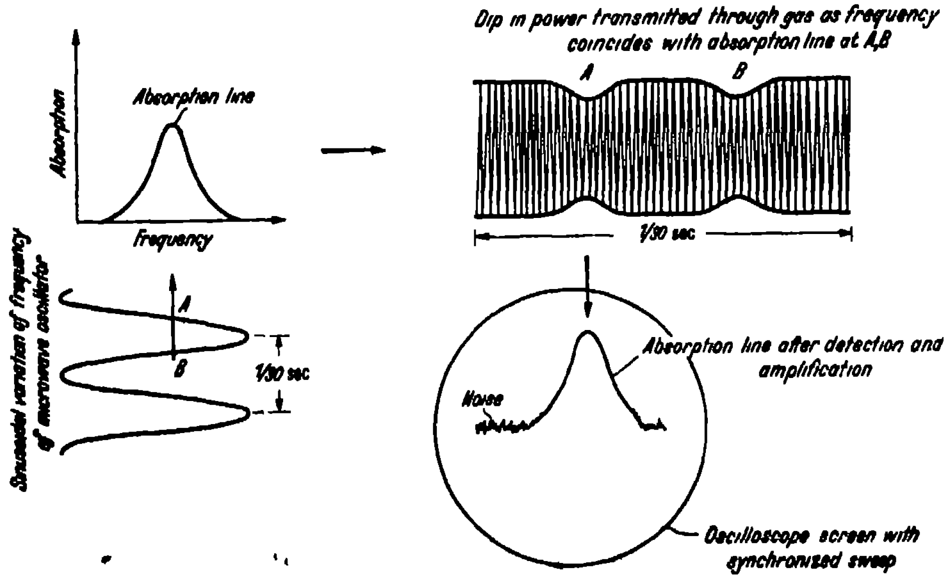
Dip in power transmitted through gas as frequency coincides with absorption line at A,B
A
B
Absorption
Absorption line
Frequency
1/30 sec
Sinusoidal variation of frequency of microwave oscillator
A
B
1/30 sec
Absorption line after detection and amplification
Noise
Oscilloscope screen with synchronized sweep

Figure 1 Schematic representation of the frequency modulation method for presenting microwave absorption lines on a cathode ray oscillograph screen

orientation in the field, are split into a number of components, thus diminishing the absorption at the centre of the original line and increasing it elsewhere If an alternating electric field is applied a modulation of the RF power traversing the gas is produced provided that an absorption line is present By raising the rate of alternation (from 6 kc/s to 85 kc/s have been used) the excessive detector noise can be largely eliminated, since it decreases rapidly with increasing frequency of the amplifier following the detector The present limit of observation is an absorption of about 10^{-9} per cm, or 10 per cent in 1,000 km This is still some way from the theoretical limit, largely because of noise fluctuations in the centimetre wave oscillator itself If the frequency of the oscillator is again varied slowly the spectral line can be displayed on a cathode-ray oscilloscope as before, but to obtain the greatest sensitivity it is necessary to reduce the noise by using a very narrow band-width that is, the klystron frequency is swept very slowly over the absorption line, and the latter is obtained as a trace on a recording millivoltmeter rather than on the oscilloscope

SPECTRA OF OXYGEN AND AMMONIA

Although the majority of microwave spectra arise from jumps between different rotational levels of the molecules, there are two odd spectra of particular interest, which are due to other causes The oxygen molecule contains two unpaired electron spins, giving it a magnetic moment which can interact with electromagnetic radiation These two spins can either be aligned parallel or perpendicular to the axis of the molecule, the magnetic interaction between them differs in energy by about 2 cm^{-1} (spectroscopic units*) in these two positions, since in one position the dipoles are end-on, and in the other broadside-on A subsidiary interaction with the magnetic field generated by the rotation of the molecule causes the energy difference to vary slightly with the rotational state, and an absorption band around 5 mm in wavelength was predicted by J H VAN VLECK[5] and confirmed by R BERINGER[6] The details of this band have not yet been resolved by work at low pressure, but it arouses considerable interest through the attenuation it causes in the atmosphere, amounting to about a factor ten in a kilometre The atmospheric absorption, obtained from recent measurements by H R L LAMONT[7], is shown in *Figure 2*, together with theoretical values of van Vleck

The second molecule is ammonia, which has the form of a low pyramid with the nitrogen atom at the apex and the three hydrogens forming a triangular base There are two equilibrium positions, one with the nitrogen above the plane of the hydrogens, the other with it below, separated by a rather small potential barrier As a result, the molecule is able to pass from one state to the other by turning itself inside-out like an umbrella In doing so it acts as an oscillating electric dipole with a frequency of about 23,000 Mc/s, wavelength 1 3 cm The existence of a strong absorption in this region was verified by the pioneer work of C E CLEETON and N H WILLIAMS[8] in 1934, using ammonia at atmospheric pressure

Since this was much the strongest spectrum the position of which was known to lie within the range of available oscillators, ammonia became the classic spectrum with which a number of investigators opened the attack on microwave spectra, using low pressures to obtain good resolution A considerable fine structure was discovered, due to centrifugal distortion of the molecule, which alters the potential barrier and the frequency of vibration In *Figure 3*, which shows the spectrum observed at a pressure of 1 2 mm of mercury, each line belongs to a different rotational level More resolution is obtained by further lowering of the pressure and at about 0 01 mm of mercury a hyperfine structure was discovered by W. E GOOD[10] This was attributed to a small

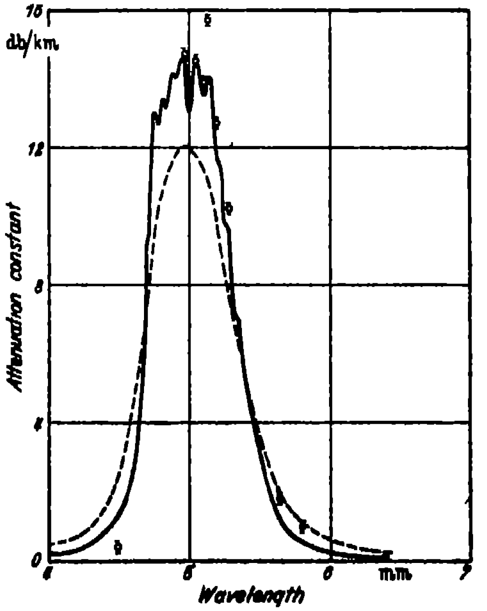

Figure 2. Absorption in the atmosphere due to oxygen, at 293°K and 760 mm mercury pressure Two theoretical curves are shown, one assuming a line-width $\Delta\bar{\nu} = 0\ 02\ \text{cm}^{-1}$, the other $\Delta\nu = 0{\cdot}05\ \text{cm}^{-1}$ (after H R L Lamont[7])

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* The spectroscopic unit of energy is the quantum $h\nu$ corresponding to a wavelength of one centimetre, i e $h\nu = hc/\lambda \approx 2 \times 10^{-16}$ ergs for $\lambda = 1$ cm, where h is Planck's constant and c is the velocity of light In these units the energy is therefore proportional to the reciprocal of the wavelength, known as the wave number, $\bar{\nu}$

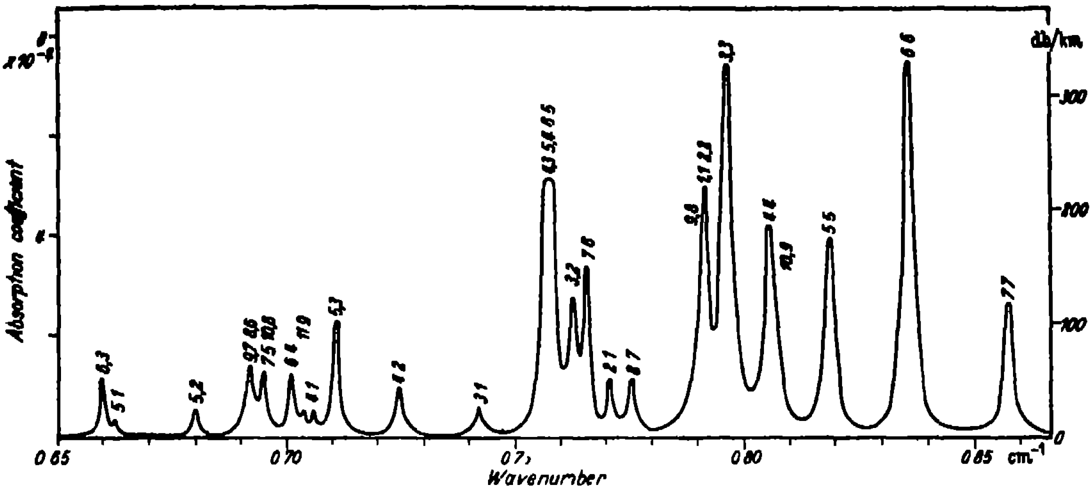

Figure 3 Absorption spectrum of ammonia at 1 2 mm mercury pressure The numbers above the absorption lines are the values of J, K $J\frac{h}{2\pi}$ is the total angular momentum of the molecule, and K determines the angle at which the axis of symmetry of the molecule moves round the vector J (after B Bleaney and R P Penrose[9])

interaction with the electric quadrupole moment, and the importance of such effects in the determination of nuclear spins is discussed later Ammonia has also been used for the study of pressure broadening[11,12], which is the dominant factor in line width, from 6 atm down to a small fraction of a mm of mercury Thus ammonia has been of great importance, though the pure rotational spectra have perhaps been more successful in yielding molecular data

ROTATIONAL SPECTRA

To have rotational transitions at frequencies below 1 cm⁻¹, a molecule must have a moment of inertia of the order of 100×10^{-40} gm cm² or more This excludes most of the simpler diatomic molecules, and triatomic molecules containing hydrogen In contrast, the heavier molecules which do not possess an axis of symmetry generally show a wealth of microwave lines which are difficult to analyse, since they arise from transitions between the irregularly spaced higher rotational levels For this reason, the bulk of investigation has hitherto been concentrated on linear molecules, notably OCS, isomers such as OCSe and the halogen cyanides, or on simple symmetrical tops such as the methyl halides and their silicone analogues (A symmetrical top molecule is one in which two of the principal moments of inertia are equal)

The rotation energy of a linear molecule is

$$E = \frac{J(J+1)h^2}{8\pi^2 I},$$

where J is the rotational quantum number and I is the moment of inertia In jumping from a state $J-1$ to J, the molecule absorbs a quantum of energy of frequency

$$\nu = \frac{E_J - E_{J-1}}{h} = \frac{Jh}{4\pi^2 I}$$

and measurement of ν therefore determines the moment of inertia, I For a number of molecules measurements have been made on a sufficient number of isotopic species of the same molecule to evaluate all the inter-atomic distances and bond angles from microwave data alone. In spite of the small fractional change in mass between the isotopes, a high accuracy can be obtained through the great precision in frequency determination This is illustrated by *Table I*, showing the various lines for OCS, as determined by C H TOWNES, A N HOLDEN and F R MERRITT[13]

Table I Frequencies for Various Isotopic Forms, OCS

Molecule	*Frequency Mc/s*
$O^{16}C^{12}S^{32}$	24,325 92 ± 0 02
$O^{16}C^{12}S^{33}$	24,020 21
$O^{16}C^{12}S^{34}$	23,731 33 ± 0 03
$O^{16}C^{13}S^{32}$	24,247 69
$O^{16}C^{13}S^{34}$	23,646 92
$O^{16}C^{14}S^{32}$	24,173 0 ± 1 0
$O^{18}C^{12}S^{32}$	22,819 30

Since only two measurements are required to determine the inter-atomic distances, a number of alternatives can be used to give a check on the theory Using four different pairs, the C—O distance is found to vary from 1 1552 to 1 1647 Å, and the C—S distance from 1 5576 to 1 5653 Å Errors in measuring the frequency could not account for these discrepancies and they are attributed to a real change in bond length for different isotopes This arises from the zero-point energy of vibration of the molecule, which changes slightly with the mass of the isotope, since this vibration means that the bond distance is never exactly equal to the equilibrium value The change in bond length with isotope cannot be determined exactly from microwave data, since for each pair of isotopic species chosen the bond lengths must be assumed identical The errors which result are generally of the order 0 01 Å

Published data on molecular structure of the methyl halides and their analogues is summarized in *Table II*, that for the chlorides[14] and 'silicyl bromide' (SiH_3Br)[15] being derived entirely from microwave data, while in the other cases a combination of microwave and infra-red data is used[16, 17]

Table II Molecular Structure of the Methyl Halides and their Analogues

Molecule	H – X *distance* Å	*Halogen* – X *distance* Å	HXH *angle*
CH_3F	1 10$_9$ (1 07)	1 385 (1 49)	110 0
CH_3Cl	1 12 (1 07)	1 781 (1 76)	110° 50
CH_3Br	1 10$_4$ (1 07)	1 936 (1 91)	110° 15
CH_3I	1 10$_9$ (1 07)	2 139 (2 10)	110° 58
SiH_3Cl	1 50 (1 47)	2 048 (2 16)	110° 57
SiH_3Br	1 57 (1 47)	2 209 (2 31)	111° 20′
GeH_3Cl	1 52 (1 52)	2 147 (2 21)	111° 4′

X denotes C, Si or Ge Distances in parentheses are the sum of covalent radii

These data show that the HXH angle differs but little from the tetrahedral angle, 109° 28′, and the hydrogen-carbon distance is practically equal to the sum of the covalent radii, the agreement being still closer if L PAULING's[18] covalent radius for the carbon atom 0 77 Å is increased to 0 79 Å, as has been suggested by W J GORDY[19] This would also reduce the discrepancy in the carbon-halogen distance, except for the halides containing fluorine The latter is the most electronegative of all elements, however, and one may expect a considerable bond shortening due to resonance with ionic structure With silicon and germanium the halogen bond shortening has been attributed to an admixture of ionic and double bond character[14]

NUCLEAR QUADRUPOLE EFFECTS

In atomic spectra the development of spectrometers with resolving powers of the order of 100,000 to 1,000,000 revealed the presence of hyperfine structure, and made it necessary to attribute to the nucleus a spin, measured as in the atomic case in units of $h/2\pi$ Associated with this spin is a magnetic moment some 2,000 times smaller than the electronic magnetic moment owing to the heavier mass of the nucleus and the lower angular velocity for a given angular momentum Magnetic interaction between the electrons and the nucleus gives rise to a splitting of the order of 10^{-1} cm^{-1} If such an effect were present in molecules microwave spectroscopy would be an exceedingly powerful tool for its analysis, since splittings of this order could be determined with an accuracy of about 1 in 10^5 Such magnetic interaction is absent, however, since the electronic shells of nearly all molecules contain no unpaired electrons, and hence have no magnetic moment An exception is O_2, but normal oxygen of mass 16 has no nuclear spin, if the rare isotope of mass 17, which has a spin $\frac{1}{2}$, is used, a considerable hyperfine structure should be observed Infra-red spectroscopy has therefore only been able to contribute to the determination of nuclear spins through the alternating intensities they produce in band spectra

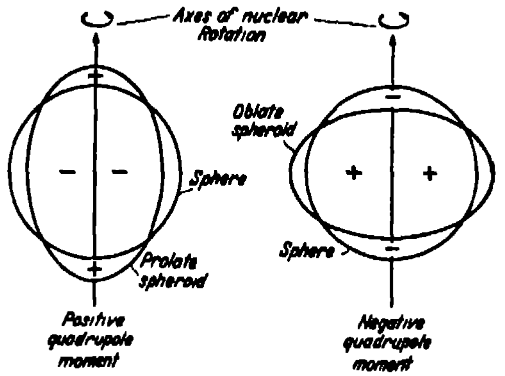

Fig 4 Representation of non-spherical charge distribution in nucleus as combination of sphere and quadrupole

This situation was completely altered by the discovery of Good[19] of a hyperfine structure in the microwave spectrum of ammonia The splitting amounts only to a few Mc/s (some 10^{-4} cm^{-1}), which is much too small to be detected in the infra-red The explanation of this effect[20, 21] lies in the existence of a nuclear electric quadrupole moment in nitrogen, mass 14

The existence of such a moment can be seen quite easily if the distribution of electric change in the nucleus is assumed to be non-spherical. It is generally accepted that the nucleus has no electric dipole moment, but if the shape of the nucleus is a prolate or oblate spheroid, as in *Figure 4*, it can be regarded as a combination of a sphere and a quadrupole, the sign of the quadrupole being positive

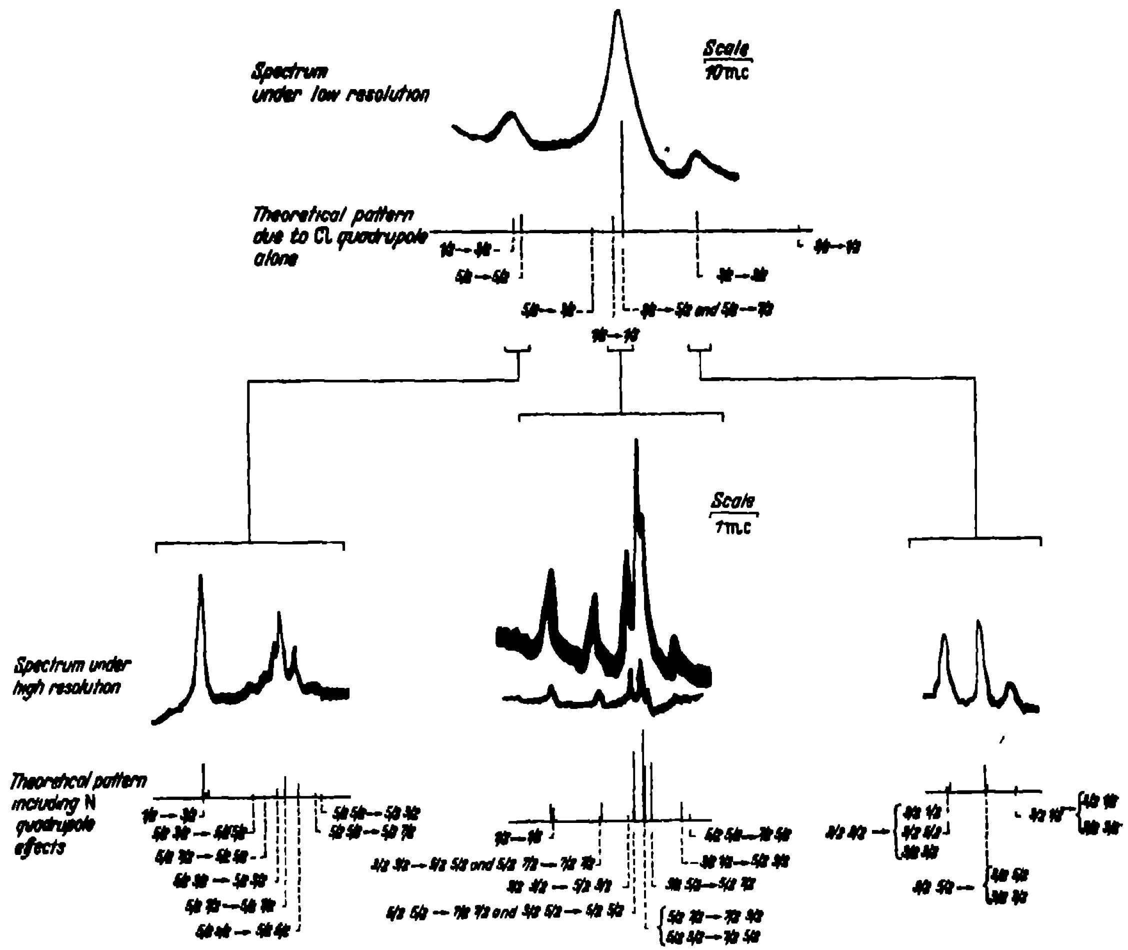

Figure 5 Complex hyperfine structure of $J = 1 \rightarrow 2$ rotational transition in $Cl^{35}CN$ *The patterns under both low and high resolution are shown, with comparison with theoretical pattern assuming nuclear spin of* Cl^{35} *is 3/2 (after C H Townes, A N Holden and F R Merritt*[19]*)*

if the nucleus is prolate and negative if it is oblate The quadrupole produces a non-uniform electric field which falls off with the inverse fourth power of the distance, and produces a very small effect on the electronic motion The magnitude of this effect depends on the magnetic quantum number M of the nuclear spin I i e the angle at which it precesses about the symmetry axis of the spheroid Since the quadrupole remains the same if reflected through the origin its interaction with the electrons is independent of the sign of M. It follows that such effects are only observable if I is 1 or more, since for $I = \frac{1}{2}$ they will be the same for both possible values of M, $\frac{1}{2}$ and $-\frac{1}{2}$

Mathematical analysis shows that the interaction between the quadrupole and the electrons is proportional to the product of the quadrupole moment, eQ, and the field gradient which the electrons produce at the nucleus Since this field gradient will rotate with the molecule, the interaction depends on the angle which the nuclear axis of symmetry makes with the axis of molecular rotation i e it is a calculable function of I, J and their vector sum F For a given value of J, F can take on $2I + 1$ values, and in a rotational transition a complex fine structure is observed from which the value of the nuclear spin I can be found A complicated spectrum where two of the nuclei have quadrupole moments is shown in *Figure 5* *Table III* gives a list of nuclear spins which have been either *a* first measured correctly or *b* confirmed by microwave spectroscopy

The last three atoms in this table are radio-active, and illustrate a valuable feature of the method in that only very small quantities of material are needed, the

Table III Nuclear Spins for various Isotopes

Atom and mass	*Nuclear spin*		*Reference*
	a	*b*	
B 10	3		22
B 11	3/2		22
N 14		1	20, 21
S 33	3/2		23
Cl 35	3/2		24
Cl 37	3/2		24
Ge 73	9/2		25
As 75		3/2	26
Br 79		3/2	24
Br 81		3/2	24
I 127		5/2	27, 28
S 35	3/2		29
Cl 36	2		30
I 129	7/2		31

observations being necessarily made at pressures of the order of 0·01 mm of mercury. It should be noted also that in a number of other cases, for example[32], S 34, Se 74, 76, 77, 78 and 80 the absence of any observable hyperfine structure leads to the conclusion that the spin is 0 or ½, according to whether the nuclear mass is even or odd. Of course such negative evidence may not be final and the value of ½ for Se 77 has been queried by J. E. MACK[33].

Although the spin is determined unequivocally from the nature of the hyperfine structure (apart from the exceptions mentioned) the magnitude of the quadrupole moment is not, although the quantity $eQ(d^2V/dx^2)$ can be measured accurately. The difficulty lies in estimating the electric field gradient at the nucleus, d^2V/dx^2, which depends on the electron cloud distribution in the molecule. This varies considerably according to whether the binding is ionic or covalent; for example a pure ionic binding resulting in a closed shell of electrons round the nucleus would make d^2V/dx^2 zero.

Townes has pointed out that reasonable estimates of the field gradient can be made for pure covalent binding with a *p*-orbital, using atomic data. Furthermore, the magnitude of the observed hyperfine splitting can be used to estimate the ionic and covalent contributions to a hybrid bond[34]. Thus the development of an adequate theoretical treatment of this topic would assist in the determination both of nuclear and of chemical bond data.

CONCLUSION

From this brief review it is apparent that microwave spectroscopy has already been of great service to the nuclear physicist and to the structural chemist. Hitherto it has been confined to molecules with fairly simple structure, since otherwise the mathematical difficulty of the exact analysis required becomes immense. This feature seems likely to continue in the immediate future, and to result in the use of compounds which are evil-smelling or explosive (or both) as the physicist strives to incorporate new nuclei in molecules with a reasonable vapour pressure. If methods for very rapid preparation of suitable molecules are developed, the spins of radioactive nuclei of fairly short half-lives can be determined. One may note here that the discovery of hyperfine structure in the solid state by R. P. PENROSE[35], using the method of paramagnetic resonance, is likely to afford a complementary microwave method for the spins of nuclei not easily accessible to the gaseous technique. The spectroscopic values for Cu 63 and 65, Co 59 and Mn 55 have already been verified by this method[36–38].

The paramagnetic resonance method involves transitions between the different orientational energy levels of an ion in a magnetic field, i.e. it is a Zeeman effect. Magnetic fields have not been used much in gaseous spectroscopy, since only very small splittings are produced by their effect on the nuclear magnetic momenta. C. K. JEN[39] has investigated the complicated spectrum produced by a magnetic field when an initial hyperfine structure due to the electric quadrupole interaction is present, and W. GORDY, O. R. GILLIAM and R. LIVINGSTON[40] have used this method to determine the ratio of the nuclear magnetic moments of I_{129} and I_{127}.

The electric dipole moment of a molecule may be determined from the Stark splitting of its spectrum line, provided that a uniform electric field can be applied. This method has been used with a number of molecules by C. H. TOWNES, R. G. SHULMAN and B. P. DAILEY[41]. The Stark pattern is also of great assistance in sorting out complicated spectra from asymmetrical top molecules, such as sulphur dioxide[42].

Another aspect of microwave spectra which will occur to the reader is the possibility of their use for spectroscopic analysis. In this connection a table of microwave lines, containing their frequencies, intensities and other relevant data, is being prepared by C. H. TOWNES and P. KISLIUK, and will be published by the Bureau of Standards. Since no data are yet available on more complex polar molecules, which generally will have very many lines in the microwave region, it seems that the simplest analytical use would be to detect the presence of small concentrations of a given substance. This would enable the search band to be restricted very considerably, and the highest sensitivity maintained, which otherwise is difficult in sweeping over a wide frequency range. In assessing the value of this method an important difference must be noted depending on whether the substance under investigation is admixed with other gases or not. In the latter state it is a feature of pressure broadening that the intensity at the centre of the line is independent of the pressure as the pressure is reduced, the only effect on the line is that its breadth decreases in proportion This situation holds until other causes of broadening become important at about 10^{-3} mm of mercury below which pressure the width will remain constant and the intensity decrease If the substance is mixed with other gases, and the total pressure altered, the same behaviour holds, but the intensity is reduced in proportion to the fractional concentration of the substance The analysis would then be carried out at a total pressure of about 10^{-1} or 10^{-2} mm of mercury, to obtain the required resolution As an example, a spectroscope of sensitivity 10^{-8} per cm (the present limit) could detect OCS present in other gases in a relative concentration of 2×10^{-6}, if the foreign gases are non-polar and hence produce less broadening this figure could be improved by a factor ten or so

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Recent Advances in Estimation of Vitamins A

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The fat-soluble vitamin A family is mostly assayed by physicochemical means although bio-assays are still necessary for certain work The chemical and biological methods in use today have been evolved in countless small steps by numerous workers. Some of the more recent steps are discussed in the present article.

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SYNOPSIS OF PHYSICOCHEMICAL ESTIMATION

Chemical assay of the vitamins A in biological material is done in five stages comminution of the tissue, extraction of the vitamin into a convenient fat solvent, transference to a more suitable solvent for its estimation, removal of interfering substances, and absorptiometry or colorimetry Sometimes the first is unnecessary or the first and second are done concurrently, and in a few methods the third is unnecessary In special cases the fourth is omitted The last stage covers ultraviolet absorptiometry and includes preparing a coloured derivative where necessary The vitamin A family comprises two groups axerophthoids (of animal origin) and carotenoids (of plant origin) Although the same broad principles of analysis apply to each group, details differ, the groups are therefore treated separately

CHEMICAL DETERMINATION OF AXEROPHTHOL

Oils rich in vitamin A_1 may be dissolved in chloroform or other fat solvent for direct determination but most oils must first be saponified to remove interfering fat[1] Published methods for saponification usually begin by heating with ethanol and aqueous potassium hydroxide[1], these methods have not changed much in twenty years

Other material than oils must be disintegrated before the vitamin can be extracted The commonest procedure is digestion with alkali, which both breaks up the tissues and saponifies fats, followed by extraction with ether, the ether is then evaporated and the residue is dissolved in chloroform The method of hand grinding, sometimes with sodium sulphate to abstract water, has always had its supporters The Waring blender is coming into increasing use for comminuting tissues, but the homogenate or its extract often requires saponifying to remove fat, and, according to S Y THOMPSON, J GANGULY and S K KON[2], 'blending' must be done in an inert atmosphere G H BENHAM[1] discussed the accuracy of vitamin A determination and gave a useful bibliography He considered that inaccuracy was due less to destruction of the vitamin than to faulty extraction, incomplete separation of liquid phases and inadequate washing of the sodium sulphate used in drying ethereal solutions Full details of several techniques for extracting vitamin A have been given in textbook form[3] Detailed directions for extracting and estimating vitamin A are also given by W J DANN[4], a pioneer in this field

In blood the vitamin is believed to be combined with protein. The combination is easily broken with ethanol after which the vitamin may be extracted into light petroleum and chromatographed. Hence treatment of blood fractions with ethanol and light petroleum forms the basis of most methods, for instance that of S YUDKIN[5] Milk may be treated similarly to blood[6] A method for estimating vitamin A in a single drop of blood has been described[7]

COLOUR REACTIONS OF VITAMIN A

The vitamin having been brought into solution in chloroform is next assayed by physical means The method of estimating vitamin A_1 by the blue colour produced with Carr-Price reagent (antimony trichloride in chloroform) is still widely used in spite of disadvantages The reagent emits corrosive fumes With moisture it forms opaque deposits on cuvettes The colour quickly fades but the maximum can be detected photoelectrically Various authors recommend storing the antimony trichloride reagent in amber bottles although J R EDISBURY[8] indicated that colourless bottles shrouded in black paper cause less spoilage H TASTALDI[9] found that reagent concentration, temperature and other factors were not critical but that the chloroform must be pure if used more than two weeks after distillation great errors may result

A E SOBEL and H WERBIN[10] proposed the use of glycerol dichlorohydrin (1,3-dichloro-2-hydroxypropane) which forms a purple colour (maximum absorption at 555 mμ) with vitamin A_1 and its congeners The reagent is unaffected by moisture, is not corrosive, and the colour persists for ten minutes These three considerable merits are partially offset by five lesser demerits the reagent must be activated by distilling from antimony trichloride, the activity varies with time and among batches, the colour intensity is one quarter of that produced by antimony trichloride, and it requires three minutes for development D D PENKETH[11] avoided distillation from antimony trichloride by simply adding hydrochloric acid, he considered that the activation was caused by hydrogen ions By using both antimony trichloride and 1,3-dichloro-2-hydroxypentane together the permanence of the blue colour has been increased[12]

With neither reagent is the colour specific to vitamin A but colours are given with carotenoids and other compounds present in the fat-free extract or unsaponifiable fraction, although Tastaldi claimed to remove interfering substances from shark liver oil by a saponification technique M LODI[13] removed impurities from the unsaponifiable fraction of margarine by crystallization from methanol at low temperature The fact that several procedures have been proposed[14–17] to correct for the contribution by carotenoids suggests that correction is unsatisfactory. This is partly because the magnitude of the correction varies with the source of the extract. The problem is presented in severe form in butter and mixed feeds The better procedure is not to correct for carotenoids but to remove them, then to isolate carotene and determine it separately from preformed vitamin A. For this purpose carotenols (hydroxycarotenoids) are easily separated from vitamin A esters Esters can be hydrolysed and the free vitamin A separated from carotene Carotenols are not so easily separated from free vitamin A for both have similar adsorption affinities, but they have been separated by applying rigorous care Various chromatographic procedures have been proposed for these separations, such as chloroform in light petroleum with defatted bone meal[18], alumina[19], and calcium hydroxide[20] M L Cooley, J B Christiansen and R C Koehn[21] assumed that vitamin A is present wholly in ester form and separated it from carotenoids with magnesia H R Cama and T W Goodwin[22] measured the antimony trichloride blue at 617 mμ at which wavelength β-carotene is excluded , there is however risk of damage to the spectrophotometer by antimony trichloride fumes

Other colour tests for vitamin A have been proposed including the use of diphenylamine with ferric chloride[23], 'acid earths' and superfiltrol*[24] P Meunier[25] studied the theory of colour production by the vitamins A He suggested that the colour is produced by the shift in conjugated double bonds when the chromogen combines with the substances mentioned above A history of colour tests[26] appeared in 1946 In spite of disadvantages the antimony trichloride test remains the most popular and according to some workers[16, 27] is more accurate than other tests, including ultraviolet absorption, for certain oils and foods M E Chilcote, N B Guerrant and H A Ellenberger[28] compared the antimony trichloride, dichlorohydroxypentane, ultraviolet and rat growth methods for twenty eight fish oils Their tables offer a rich substrate for statistical analysis

ULTRAVIOLET SPECTROMETRY

The principal alternative test for determining vitamin A in solution uses the absorption of ultraviolet light (at 328 mμ) Photographic recording of the absorption is tedious and not so accurate as photoelectric The Beckman quartz spectrophotometer has facilitated the application of ultraviolet methods Although all *-trans* carotenoids cause negligible interference, other substances present in the unsaponifiable fraction of fish oils absorb ultraviolet light, which complicates vitamin A determination By measuring the extinction at wavelengths at which the absorption by other substances is much greater than by vitamin A, one, on each side of 328 mμ, R A Morton and A L Stubbs[29] corrected for the so-called irrelevant absorption Later B L Oser[30] proposed a simpler alternative procedure Ultraviolet light destroys vitamin A , this fact has been exploited[31,32] by measuring the extinction before and after prolonged irradiation and taking the difference, thereby allowing for unspecific absorption J Awapara, F H Mattson, J W Mehl and H J Deuel[33] determined the extinction of a crude extract, removed vitamin A on floridin, re-determined the extinction and estimated vitamin A by difference Ideally, interfering substances should be removed before determining the vitamin A and this is most cleanly done chromatographically N T Gridgeman, G P Gibson and J P Savage[34] used alumina and polar solvents to separate unsaponifiable components seriatim into up to thirty four fractions Each fraction was spot tested with antimony trichloride and those contiguous fractions giving the proper vitamin A blue were pooled for ultraviolet extinction measurement A similar method[35] used weakened alumina and light petroleum instead of polar solvents The geometric method is quicker but the separation method is more exact provided the manipulations are skilfully performed

Sometimes it is desirable to estimate the free alcohol (axerophthol) and the esterified forms of vitamin A separately The method of partition between light petroleum and aqueous alcohols is obsolescent H Sobotka, S Kann and W Winternitz[36] exploited the different rates of fading of the fluorescence of the alcohol and the ester to determine their proportions Other workers have separated the two forms chromatographically using for instance alumina with polar solvents in light petroleum[16, 37-40], bone meal with chloroform in light petroleum followed by acetone[41], and magnesia with chloroform in light petroleum[42]

Vitamin A_2, which occurs in the livers of certain fresh water fishes and which has been isolated and studied by E M Shantz[43], can be estimated similarly to vitamin A_1 except that the antimony trichloride colour or the ultraviolet absorption must be measured at different wavelengths from those associated with vitamin A_1

EXTRACTION OF CAROTENE

The technique of carotene estimation has changed radically during the past eight years A major revolution concerns extraction The once popular alkaline digestion, with its danger of destroying carotene, is passing into desuetude Vegetable tissue is now macerated mechanically and the carotene is extracted directly into acetone, ethanol, light petroleum or into mixtures Heat is desirably avoided at all stages because it favours isomerization *Cis* isomers of the carotenes have lower extinctions

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* Superfiltrol is a commercial adsorbent made from aluminium silicate

(colour intensities) than the predominantly occurring all-*trans* forms. Isomerization would therefore result in underestimation of the original carotene.

New methods or modifications for carotene determinations are frequently proposed. Many are too lengthy for regular use. One of the simplest is that in which very small samples are quickly ground with quartz under a mixture of light petroleum, acetone and quinol in a small beaker[44]. The Waring blender and its imitators are much used, a popular method being that of L A MOORE and R ELY[45], who extracted with a foaming mixture of ethanol and light petroleum. Disintegration and extraction were achieved concurrently in the blender and the foam minimized splashing. Although the blender eliminates hand grinding, Moore's application of it involves so many manipulations of solutions, since ethanol is difficult to remove cleanly from light petroleum, that in a comparative test V H BOOTH[46] found the beaker method considerably faster in preparing extracts. Acetone is preferable to ethanol for subsequent removal from light petroleum and has been used in the blender[47], but, in the author's experience, acetone leads to destruction of carotene during blending. Evidence has also been found of oxidation of protein[48] during homogenization in the blender. Nevertheless, used with circumspection, the blender is invaluable for large or bulky samples. More carotene was extracted from alfalfa meal[49] in a Bailey-Walker apparatus than by one method[50] using a blender. The water present in biological material hinders extraction but may be withdrawn by grinding with anhydrous sodium sulphate. This well known trick, in spite of the hard work it involves, has been adopted by many including T B MANN[50] and B BENCZE[51]. A SREENIVASAN and R M VAIDYA[52] ground leaves with quartz and cyanide, then added anhydrous sodium sulphate and ground again, pigments were extracted with warm light petroleum. The same values were found for carotene in leaves by this method as by that of M E WALL and E G KELLEY[50]. H. W BERKHOUT and G H JONGEN[53] have described a machine for eliminating hand grinding which avoids such disadvantages of the blender as having the cutter shaft pass through the bottom of the macerating vessel. Biochemists however are usually shy of apparatus which brings vitamins into contact with copper, and one would like to see the apparatus made of stainless steel.

In the tunnel technique for carrots[44] small cylinders were removed with a borer, measured and quickly extracted with cold petrol-acetone by grinding with quartz in small beakers. Measuring is quicker than weighing and equally accurate, and because the carrots survive the assay they may be replanted for seed production.

Carotene, however extracted, is required in light petroleum for subsequent treatment. Generally this necessitates removing acetone or other polar solvent. Some workers evaporate and re-dissolve in petroleum, although this is risky because carotene is vulnerable to oxidation when out of solution. Water-soluble solvents may be washed away leaving pigments in light petroleum, but washing by shaking solutions in separating funnels is laborious and entails some loss although it is still being recommended. A L LEROSEN[54] designed an attachment for converting separating funnels for automatic washing. An S-tube[44] is simpler and avoids risk of loss through air leaks.

Green leaves contain a system which destroys carotene when the leaves are damaged and up to one quarter of the carotene may be lost from pulped leaves in six minutes[44]. Relatively few authors recognize that precautions should be taken to prevent losses during manipulations, although some recommend blanching (immersing in boiling water). In the author's experience blanching is not only unnecessary when extraction is done immediately with petrol-acetone-quinol but, if continued for more than two minutes, may destroy some carotene.

EXTRACTION FROM DRIED GREEN CROP MEAL

Because prices of dried grass and lucerne (alfalfa) meals are based upon their carotene content much attention has been paid to its estimation. The greater difficulty of extracting carotene from dried than from fresh leaves has been discussed by F P ZSCHEILE and R A WHITMORE[47], who modified M E WALL and E G KELLEY's [50] method, and by V H BOOTH[46]. The simplest technique for extracting dried leaf meal is to soak it in light petroleum for two days or longer. So much time however can ill be spared. A rapid yet elegantly simple technique has been devised by J R EDISBURY and tested by a collaborative committee[56]. The meal is heated with petroleum of boiling range 80 to 100°C in a long necked flask on a water bath at 90°C for an hour, cooled, and the extract decanted directly on to a chromatographic column. There is no polar solvent to be removed.

CHROMATOGRAPHIC ADSORPTION ANALYSIS

The other major revolution in carotene estimation was the supercession of phasic separation by chromatography for removing non-carotene pigments. Chromatography is more specific in its separation of the pigments, is faster than phasic separations and saponification of extracts is usually unnecessary. Several adsorbents are in use. Dicalcium phosphate[57] is popular, and bone meal[58] behaves similarly. Kieselguhr[59] is readily available although its speci ficity is low Calcium hydroxide was preferred by M VAN EEKELEN, C ENGEL and A BOS[60] who compared it with other adsorbents B BENCZE[61] preferred calcium carbonate O. RIBEIRO[62] prepared a magnesium carbonate which separated lycopene from carotene *Magnesia and alumina are more specific* in removing non-carotene pigments Alumina is hygroscopic and moisture affects its adsorptive power but it may be stabilized by mixing with anhydrous sodium sulphate[63] Magnesia is one of the most convenient adsorbents for separating α-, β- and γ-carotenes as well as for distinguishing between their *cis-trans* isomers

Percolation through some powders is too slow for routine determinations even when suction is used The rate may be increased by admixing a filter aid *e g* kieselguhr, or, where dilution cannot be tolerated, by applying gas pressure above the column[61] Alternatively, radial percolation can be hastened in the chromatofuge[62] by leading the solution into the centre of a rotating drum of adsorbent

In one variant of the chromatographic technique for purifying carotene the pigments are all adsorbed at the top of a tube of powder, and carotene is then eluted as a separate visible band by a polar solvent such as benzene or acetone dissolved in light petroleum In another variant only the non-carotenes are adsorbed while carotene passes straight through into the filtrate this method is the simpler but it is not so easy to see what is happening

A recent booklet[63] provides an excellent introduction to chromatography and contains a useful bibliography H H STRAIN[64] has reviewed recent progress in chromatography An examination of several developers indicated that anethol in light petroleum[65] produced the widest separation of carotenes on a chromatographic column

SPECTROPHOTOMETRY

The vitamin, or a coloured derivative, being in solution is best determined absorptiometrically or colorimetrically R. J TAYLOR[66] has written a dissertation on abridged spectrophotometry with special reference to carotene determinations in a plunger colorimeter However the commonest type of abridged spectrophotometer for vitamin A and carotene determinations is the photoelectric absorptiometer using a filter. Photoelectric colorimeters are not so foolproof as visual instruments but they obviate observer errors in colour matching Null point or compensated twin photocell instruments, despite apparent advantages, are not so favoured as direct reading instruments The latter are invaluable for detecting the maximum for a quickly fading colour such as axerophthol antimony trichloride blue

Dye filters pass a wider spectral band than desirable Consequently edge-light passes through the vitamin solution and the overall response is not linear, thereby limiting the measurable range of concentrations Interference filters pass a narrower waveband, but they must be accurately mounted and illuminated with parallel light Each vitamin requires a specific filter However an alternative to a set of filters is a diffraction grating of which the spectral selectivity lies between those of the dye filter and the interference filter and which supplies light of any desired mean wavelength by turning a knob

Where much narrower spectral bands are required, for determining absorption curves or for distinguishing between such similar pigments as α- and β-carotenes, a prism spectrophotometer is required Visual and photographic instruments are being displaced by photoelectric spectrophotometers The current from a photocell illumined with the small light flux in a narrow spectral band cannot be detected directly but must be amplified The Beckman *DU*, the *Unicam* and the Hilger *Uvispek* are null point amplifier spectrophotometers of this type and can be used over the approximate range 200 to 800 mμ

CALIBRATION AND CONVERSION FACTORS

Non-absolute instruments (abridged spectrophotometers) must be calibrated, preferably with pure axerophthol or its acetate, or phenyl azo-*p*-cresol[67], and with carotene respectively Pure β-carotene is the obvious calibrant for the latter group but it is tedious to prepare and there is danger[68] of its absorbing alcohols of crystallization unless rigorously dried Fortunately commercial preparations containing 88 per cent β- and 11 per cent α-carotene are easily obtainable and are satisfactory for calibration Individual absolute instruments (spectrophotometers) need no calibrant, the conversion of extinctions to international units (I U) or mg being a matter of simple proportion given the extinction of the appropriate pure vitamer An acceptable value for the extinction (E, 1 per cent 1 cm, 450 mμ) of β-carotene in hexane is 2,500, although as technique improves and purity increases this value rises and the true value probably approaches 2,600 The controversy on the conversion factor (extinctions to I U) for axerophthol has been discussed by N T. GRIDGEMAN[69] and by H. A. ELLENBERGER, N. B GUERRANT and M E CHILCOTE[70] who give references to other discussions. It is earnestly hoped that a definitive factor has been agreed upon at the recent meeting of the international standards committee the report of which is awaited with interest.

LIMITATION OF CHEMICAL ASSAY AS CRITERION FOR BIOLOGICAL VALUE

One problem in the chemical estimation of vitamin A is posed by the very extensiveness of the family of A-vitamers The family includes axerophthol (vitamin A_1) and its esters, vitamin A_2, the retinenes, numerous synthetic derivatives, three carotenes, several hydroxycarotenoids and their esters, and possibly other compounds not yet characterized (P Le Gallic[71] for instance postulated in rat blood a vitamin A active substance which is not detected by the usual chemical tests) Moreover each of these compounds may exist in several *cis-trans* forms, some of which have been isolated by L Zechmeister[72] and others The biological activity varies from vitamer to vitamer Fortunately the all-*trans* forms of axerophthol (and its esters) and of β-carotene predominate in nature Hence the concentration of axerophthol and/or β-carotene usually provides an estimate of the vitamin A value of a food Nevertheless certain foods may contain other vitamers *e g* α-carotene, kryptoxanthol, vitamin A_2, which may or may not be excluded by the analytical technique Alternatively part of either may be present in a *cis* form having low biological value The obvious course for calculating vitamin potency is to analyse the mixture and sum the products of the concentration of each vitamer by its vitamin A value A beginning has been made for carotenoids[73, 74] but for axerophthoids the procedure is only hinted at[76] The procedure is complicated and, through losses in chromatographic separation of small quantities, uncertain biological values *etc* the accuracy attainable scarcely justifies its use

BIO-ASSAY OF VITAMIN A

Another approach to the problem of determining the vitamin A potency of a complex is offered by the biological test The rat growth method is most commonly used for vitamin A (here used in its general sense to embrace all A vitamers including active carotenoids) This method is described by K H Coward[75] and although improvements have been adopted the principle has remained the same for many years A noteworthy change is the insistence on giving the rats adequate vitamin E to fulfil the standard requirement of vitamin assays that the basal diet shall contain optimal amounts of all known essentials except that under test without this precaution one may be measuring not vitamin A in the test substance but the combined effect of vitamins A and E owing to their *synergy*[76] K Guggenheim[77] purposively measured this combination by the rat liver storage method and listed biological values for the carotene in various foods It would however be more useful to evaluate vitamins A and E separately Chicks have been claimed to compare favourably with rats in growth methods[78, 79]

The computations for the bio-assay[75,80,81] are based on comparing the difference in response between two suboptimal doses of the unknown with the difference in response between two suboptimal doses of the standard

N T Gridgeman[81] gave a detailed criticism of the bio-assay For forty rats per growth test dosed for four weeks he assessed the limits of error (at *P* = 0 95) at 67–149 per cent He considered that ultraviolet spectrometry is better than bio-assays for routine estimation of vitamin A in fish oils Nevertheless the relative vitamin A activity of the derivatives and isomers of axerophthol and of β-carotene, natural or synthetic, must be determined biologically Moreover the vitamin value of any of these vitamers as they occur in foods is not always the same as in oil and can only be found by biological test

There are alternatives to the growth method J Mayer and W A Krehl[82] found that the growth efficiency *i e* weight gained per weight of food eaten, is so regular an index of vitamin A deficiency that its measurement might serve as a basis for bio-assay Alternatively the axerophthol in rats' livers may be determined after ingestion of the test material The method has been used for comparative results[77,83–85] and details of one technique have been given by K Guggenheim and W Koch[86] J R Foy and K Morgareidge[87] compared it advantageously with growth tests for fish oils Liver method rats are healthy because the vitamin A intake is optimal whereas in the growth test the doses are suboptimal and the rats are vulnerable to infection which makes response erratic Moreover, the basal diet need not be so rigorously free of vitamin A, neither dosing date nor level is so critical as in growth tests, and dosing may be completed in a shorter time A disadvantage of the liver method is that very large doses are necessary and this excludes any but rich materials It is well established that α-carotene and kryptoxanthol have half the vitamin activity of β-carotene in growth tests On the other hand R M Johnson and C A Baumann[88] observed that α-carotene had 25 per cent and kryptoxanthol had 100 per cent of the liver storage activity of β-carotene (Other references are given[89]) Moreover the vitamin A value of carotene in carrots[83] is about half that of carotene in oil when growth is the criterion but about equivalent when liver is the criterion Further there may be many substances which, like vitamin A acid[90], support growth but do not lead to liver storage. Nevertheless the advantages of the liver method warrant its development to overcome the disadvantages and to elucidate these anomalies

It is universally agreed that neither the international standard β-carotene nor the *U S Pharmacopeia* reference cod liver oils are satisfactory standards Axerophthyl acetate is already used in U S A and elsewhere as an alternative to β-carotene Agreement is urgently needed on how much of this standard comprises an international or other unit

Ultimately the knowledge of vitamin values of foods is usually required for application to human needs It is doubtful whether findings with rats can be exactly applied to man Man is the obvious experimental animal and in spite of grave disadvantages has been used for vitamin studies In a carefully written report of a large scale experiment, E M HUME and H A KREBS[31] concluded that dark adaptation and rod scotometry are the best criteria for assessing vitamin A status in man

ESTIMATES OF ACCURACY AND DESIGN OF EXPERIMENTS

Ten years ago the only statistic usually calculated from chemical assays of vitamins was the mean, although relatively elaborate computations were made to obtain the mean from bio-assays Now it is recognized that the mean is not enough and even a statement of the range of values is of little more use An evaluation of variation among samples is required and statistical tests of the significance of differences between means are regularly made Experiments can be, and nowadays should be, so designed as to facilitate computing these statistics Moreover in a properly designed bio-assay fiducial limits of error are computed for a given level of probability Future trends will doubtless be towards ever more exact assessment of the accuracy of published values

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Stereochemistry of Cyclohexane

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Substances containing six-membered rings the atoms of which are linked together by single bonds occur in nature, and many of them are of considerable importance to biochemistry A detailed knowledge of the steric configuration of this class of substance is of fundamental interest, however, not only to biochemistry but to chemistry in general

If the van't Hoff-Le Bel concept of the tetrahedral valency angles of carbon is accepted, it is clear that the carbon ring in *cyclo*hexane cannot be planar but that we have to accept the models discussed by Sachse and by Mohr We are therefore concerned with two possibilities *1* a 'rigid' centrosymmetrical ring, the 'staircase' or 'chair' form, and *2* a 'movable' form which in one extreme position is well known to all chemists as the 'tub' or 'boat' form

Although chemists seem to have accepted these ideas about the carbon skeleton of *cyclo*hexane and its derivatives the discussion of stereoisomerism has generally been based on the concept of a planar ring; it must be admitted that no serious difficulties in explaining the number of stereoisomers corresponding to a given structural formula have thus arisen This of course is the chief reason why organic chemists until recently have not been very much interested in a more detailed study of the stereochemistry of *cyclo*hexane and related substances

INITIAL RESEARCHES

The first instance in which modern physical methods yielded more direct information on the spatial arrangement of the atoms of a *cyclo*hexane derivative was that of β benzene hexachloride and the corresponding hexabromide Here[1] x-ray crystallographic examinations suggested very strongly that the carbon ring has a form very similar to that of the 'staircase' model and that the remaining valency angles are also distributed in conformity with that model S B Hendricks stressed the necessity of a revision of the general treatment of the stereochemistry of *cyclo*hexane, but even in the following years the question was given very little attention by chemists in general. The author and his co-workers[2] and other chemists, however, working with x-ray and electron diffraction methods and measuring dipole moments, gathered experimental material concerning *cyclo*hexane and its derivatives. They interpreted these results in such a way that by the end of the nineteen thirties very little doubt still existed as to the general correctness of the Sachse-Mohr picture of the *cyclo*hexane ring.

The most striking feature of the results obtained at that time was, in the author's opinion, the fact that no indication of the occurrence of the 'movable' form of the *cyclo*hexane ring had been found. New measurements of *cyclo*hexane vapour using the electron diffraction method based on a rotating sector also failed to reveal the existence of molecules which did not correspond to the 'staircase' model[3]. In 1943[4] it was pointed out that this may be explained by the fact that in a movable form the hydrogen atoms will come closer to each other than may be energetically favourable or even possible if tetrahedral valency angles are maintained. It was suggested that the energy of a *cyclo*hexane molecule based on a carbon ring of the 'movable' type may be high enough to make the concentration of such molecules very small in the vapour or in the liquid phase.

Another aspect of the *cyclo*hexane problem which was considered in the paper just mentioned is the following: even if the 'movable' forms of *cyclo*hexane molecules or its derivatives are disregarded it must be borne in mind that the six carbon atoms forming the carbon ring of the 'staircase' form are situated in two planes, each plane containing three carbon atoms, the distance between the two planes being about 0.5 Å. If the three carbon atoms of the lower plane are moving upwards, the three atoms of the higher plane downwards, the two planes may interchange their positions and the molecule appear in a second 'staircase' form which may or may not be geometrically identical with that of the original molecule depending on its original geometrical properties. It is easily seen that a molecule of *cyclo*hexane itself is not changed in the course of a 'conversion' of this kind, but that in the majority of examples molecules of substituted *cyclo*hexanes will be different before and after the conversion has taken place. The fact that the number of separable isomers of a *cyclo*hexane derivative of given structural formula may be accounted for satisfactorily on the basis of a planar carbon ring was due to the attribution of a comparatively small activation energy to the conversion process.

TWO TYPES OF C—H BONDS

It was further pointed out that the hydrogen atoms of the *cyclo*hexane molecule in its symmetrical 'staircase' form consist of two geometrically different groups. The lines joining the six hydrogen atoms of the first group to the adjacent carbon atoms all run parallel to the principal axis of the carbon ring, whereas the angle between the C—H bonds of the remaining six hydrogen atoms and the principal axis is equal to the tetrahedral angle, 109° 28′. Each methylene group thus comprises one hydrogen atom of each kind. It was considered useful to introduce a specific designation for each of the two kinds of hydrogen atoms or the corresponding bonds in order to make possible a straightforward description of the configuration of a given *cyclo*hexane derivative. Supposing that the chief axis of the carbon ring is vertical the C—H bonds of the first group will also be vertical and these bonds were designated as *ε* bonds (from the first letter in the Greek word for 'upright'). The remaining six bonds which are not very far from being horizontal were called *κ* bonds (from the first letter in the Greek word meaning 'prostrate'). Numbering the carbon atoms as usual from 1 to 6 and indicating for each substituent whether it is of the *ε* or *κ* type, a full and condensed description of the molecular configuration can be given. It has to be admitted that mirror image forms will thus receive identical notations. This, however, is of no practical importance as long as we are not interested in absolute configurations of optically active molecules.

It is easily recognized that the 'conversion' of the carbon ring described above transforms each *ε* bond into a *κ* bond and *vice versa*. In general the geometry of the molecule will be different before and after the conversion has taken place. If we consider the changes produced in the relative positions of atoms within the molecule it is to be expected that the energy contents of the two forms will differ so much that their equilibrium concentrations in the liquid or vapour states will be far from equal.

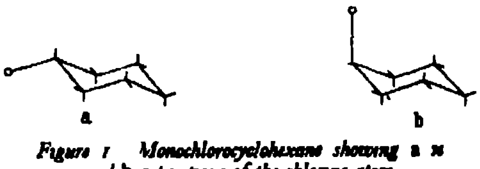

Figure 1 *Monochlorocyclohexane showing* a *κ* *and* b *ε positions of the chlorine atom*

To determine in special cases which of the two configurations predominates in the vapour state seemed to be of considerable interest. The first example investigated was that of monochloro*cyclo*hexane. Using the electron diffraction method based on a rotating sector it was possible to prove[5] that the form in which the chlorine atom occupies the *κ* position (*Figure 1*a) must be present in a concentration considerably greater than the other form in which the chlorine atom is in *ε* position (*Figure 1*b). The result of this experiment was explained as follows: if the chlorine atom occupies the *ε* position its distance from the two nearest ε-bonded hydrogen atoms would be much smaller than energetically possible if the tetrahedral angles were maintained The deformations of valency angles necessary to prevent this would probably raise the energy of this form relative to the energy of the κ chlorine form sufficiently to explain the experimental observation Some years later, in 1946, corresponding results were obtained with *cyclo*hexylthiol

The argument used to explain the stability of the κ chloro*cyclo*hexane relative to that of the ε form should also be applicable in the *trans*-1,4-dihalogeno*cyclo*hexanes (1κ 4κ ⇌ 1ε 4ε) We should therefore expect the 1κ 4κ configuration to predominate in the vapour of these substances and to be the most probable even in the solid state These expectations seem to be in full agreement with experimental results[6,7] A more complicated case is that of the *trans*-1,2-dihalogeno*cyclo*hexanes with the possible configurations 1κ 2κ and 1ε 2ε In the latter configuration the close approach of each ε halogen atom to its two nearest hydrogen neighbours should of course be unfavourable But on the other hand the distance between the two neighbouring κ-bonded halogen atoms of the former should also be expected to be shorter than energetically favourable if normal valency angles are maintained Besides the strain thus arising in the 1κ 2κ form the dipole-dipole interaction might be expected to raise the energy of this configuration The electron diffraction investigation of the dibromo-compound[8] makes us believe that the concentrations of κ κ- and ε ε-molecules in the vapour are not far from equal

Investigations based on both electron diffraction and on x-ray crystallographic work carried out more recently have indeed shown that valency angle deformations take place both when two κ chlorine atoms occur in 1,2 position in *cyclo*hexane derivatives and when two ε chlorine atoms are present In the first instance the deformations bring the two substituents further apart[8], in the second a bending of the C—Cl bond away from the chief axis of the carbon ring has been clearly demonstrated[9] Particularly large deviations from normal valency angles should be expected when two ε substituents are introduced in the 1,3 position The crystal structure analysis of γ benzene hexachloride confirms this view[10] If the substituents are fluorine, however, the deformations will probably always be small The molecular structure of dodecafluoro*cyclo*hexane for example seems to differ very little from the classical 'staircase' model based on strictly tetrahedral angles[11] In *cyclo*hexane itself the smallest hydrogen-hydrogen distance (between ε-bonded atoms in the 1,3 position) of about 2 5 Å is no doubt energetically very favourable and thus like the 1κ 2κ hydrogen-hydrogen approach contributes to the stabilization of the 'staircase' structure

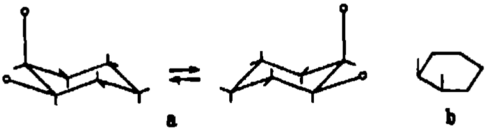

Figure 2 a *cis-1,2-disubstituted cyclohexanes corresponding to configurations 1κ 2ε → 1ε 2κ* b *model based on planar carbon ring*

POSSIBILITY OF OPTICALLY ACTIVE FORMS

As mentioned above the right number of steric isomers corresponding to a given structural formula may be deduced from a symmetrical model with a planar carbon ring If such a model contains a plane of symmetry we may conclude that the molecules corresponding to this model are not separable by chemical means into *d* and *l* forms It is easily recognized, however, that in such instances stable configurations attainable by the actual molecules, like those corresponding to models containing a carbon ring of the 'staircase' type, may often appear in two equivalent mirror image forms A conversion of the ring will then transfer the positive form into the negative form and *vice versa* Although no instance seems to have been reported in which substances belonging to this group have been observed to crystallize in enantiomorphic forms, we do not think it impossible that this may be observed in the future

The simplest representatives belonging to this group (the members of which will of course always contain an equal number of κ and ε substituents of the same kind) are the *cis*-1,2-disubstituted *cyclo*hexanes $C_6H_{10}X_2$ corresponding to the configurations 1κ 2ε and 1ε 2κ (*Figure 2*)

When the ring conversion, on the other hand, does not change the picture of an asymmetric molecule, optically active forms will be stable in the vapour phase or in solution, but then the asymmetry is preserved also in the model based on a planar carbon ring A simple example of this kind of *trans*-1,3-disubstituted *cyclo*hexanes $C_6H_{10}X_2$ (ε κ ⇌ κ ε) is visualized in *Figure 3*

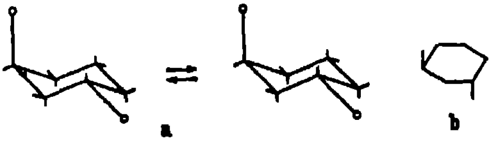

Figure 3 a *trans-1,3-disubstituted cyclohexanes corresponding to configurations 1ε 3κ → 1κ 3ε* b *model based on planar carbon ring*

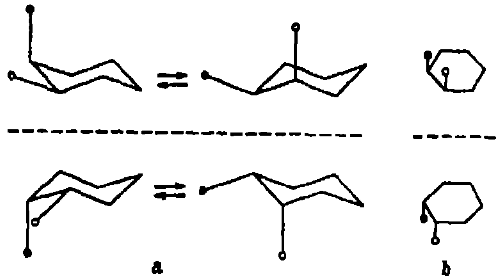

Figure 4 *Interconvertible configurations of cis-(ε κ ⇌ κ ε) 1, 2-cyclohexanes with two different substituents* b *models based on planar carbon ring*

If we return for a moment to the *cis* (ε κ ⇌ κ ε) 1,2 derivatives but this time with two different substituents (thus considering also examples in which a second, unsymmetrical ring is attached to the *cyclo*hexane ring in the 1,2 position), the picture will be representative for other more complicated derivatives of *cyclo*hexane also Here, as in *Figure 4*, the two interconvertible configurations taken together represent one optically active chemical species They may be rather different in shape, but each of them corresponds to a mirror image form of the other species The specific rotation observed for each of the two species will of course depend on the proportion of the two interconvertible configurations in the equilibrium mixture The specific rotation might then depend considerably on the medium in which the substance is dissolved if the interaction between solute and solvent influences the equilibrium concentration ratio between the two configurations Interactions, sufficiently strong and specific to modify the equilibrium, may perhaps be found where strong hydrogen bonds are being formed between the molecules of the solute and the solvent

STRUCTURE OF RINGS CONTAINING SUBSTITUENTS

The arguments used when discussing the structure of molecules containing *cyclo*hexane rings cannot of course be applied without modification to substances in which methylene groups of the six-membered ring are replaced by oxygen, sulphur, NH groups and so on Experimental results so far reported seem to indicate, however, that in 1,4-dioxane, 1,4-dithiane, *sym*-trithiane and derivatives of these substances the six-membered rings have a configuration corresponding to that of the 'staircase' form of *cyclo*hexane[12].

In 1943 O HASSEL[13] pointed to the very unfavourable hydrogen-hydrogen distances in Mohr's model of *cis*-decalin, *Figure 5*, with its two *cyclo*hexane rings of the 'boat' form and suggested that the form given in

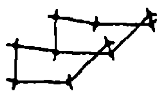

Figure 5 *Mohr's model of cis-decalin*

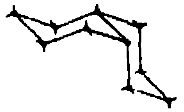

Figure 6 *Hassel's model of cis-decalin*

Figure 6 would be energetically more favourable Electron diffraction results based on the analysis of scattering curves obtained from photometer records of sector diagrams both of *trans*- and *cis*-decalin strongly substantiated this view[14] It seems justified therefore to designate *trans*-decalin as 1κ 2κ-tetramethylene-*cyclo*hexane and *cis*-decalin as consisting essentially of molecules having the corresponding 1κ 2ε structure of *Figure 6*

Now if the configurations of the two naphthodioxanes strictly correspond to those of the decalins the substance corresponding to *trans*-decalin should have zero dipole moment, whereas the second one should have a small dipole moment only Measurements carried out in our laboratory indicate that the higher melting isomer may indeed have zero moment whereas according to measurements quoted by J BÖESEKEN *et alii*[15] a moment of 0 7 D was observed X-ray crystallographic measurements have recently been carried out on the lower melting substance (m pt 111°C) obtained from 2,3-dichlorodioxane and glycol and generally believed to be a form of naphthodioxane It has been shown[16] that this substance is not a naphthodioxane but bi-1,3-dioxa*cyclo*pentyl* which contains two five-membered rings joined by a single bond Although in the crystalline state this molecule is centro-symmetric it is easy to understand that a considerable dipole moment will be observed in solution Further experimental work will be necessary, however, in order to establish with certainty whether the higher melting substance mentioned above corresponds to the *cis* or the *trans* form of decalin

Interesting problems arise when the structure of substances containing NH groups is considered The hydrogen atom of such a group or the substituent which may be introduced in its place will no doubt be able to change over from κ to ε position independently of a conversion of the six-membered ring. The N N′-dichloropiperazine, for example, should therefore in principle be capable of appearing in three different configurations in a gaseous equilibrium mixture one corresponding to the *cis* form of 1,4-dichloro*cyclo*hexane (κ ε configuration) and two to the possible configuration of the *trans* forms (κ κ and ε ε configurations) According to our experiences relating to derivatives of *cyclo*hexane we should expect the κ κ configuration to possess the

Table I Melting Point and Configuration of Isomers of Cyclohexane

Substance	*Melting point °C*	*Configuration observed*	*Physical state*	*Reference*
monochlorocyclohexane	—	κ	*v*	5
cyclohexylmercaptan	—	κ	*v*	4
1,2-dibromocyclohexane (trans)	—	κ,κ and ε,ε	*v*	6
1,3-dibromocyclohexane	48	κ,κ	*v*	2
1,3-diiodocyclohexane	84	κ,κ	*v*	3, 16
1,4-dichlorocyclohexane	102	κ,κ	*v*	2
1,4-dibromocyclohexane	112	κ,κ	*v, s*	2, 7
1,4-diiodocyclohexane	142	κ,κ	*v, s*	2, 7
1,2,4,5,-tetrachlorocyclohexane	174	ε,ε,κ,κ	*v, s*	9
1,2,4,5-tetrabromocyclohexane	185	ε,ε,κ,κ	*v, s*	17
1,2,4,5-tetrabromocyclohexane	218	κ,κ,κ,κ	*s*	20
1,2,3,4-tetrabromocyclohexane	142	κ,κ,κ,κ	*s*	21
1,1′,2,4,4′,5-hexachlorocyclohexane	145	(κε),κ,(κε),κ	*v, s*	22
α *1,2,3,4,5,6-hexachlorocyclohexane*	156	ε,ε,κ,κ,κ,κ	*v*	8
β *1,2,3,4,5,6-hexachlorocyclohexane*	308	κ,κ,κ,κ,κ,κ	*v, s*	1, 8
γ *1,2,3,4,5,6-hexachlorocyclohexane*	113	ε,ε,ε,κ,κ,κ	*v, s*	8, 10
δ *1,2,3,4,5,6-hexachlorocyclohexane*	138	ε,κ,κ,κ,κ,κ	*v*	8
ε *1,2,3,4,5,6-hexachlorocyclohexane*	219	ε,κ,κ,ε,κ,κ	*v, s*	8, 10
β *1,2,3,4,5,6-hexabromocyclohexane*	—	κ,κ,κ,κ,κ,κ	*s*	1
α *1,3,5-cyclohexantriol (dihydrate)*	—	κ,κ,κ	*s*	18
1,3,5-triaminocyclohexane (dihydrate)	—	κ,κ,κ	*s*	24

lowest energy and therefore to be present in the largest concentration Preliminary crystallographic observations indicate that this substance is isomorphous with the crystals of the *trans*-1,4-dihalogeno*cyclo*hexanes which contain molecules having the κ κ configuration[22]

CONCLUSIONS

The principles reviewed in this article should be clear enough to enable chemists to set up a complete list for substances of the *cyclo*hexane type, giving the possible number of isomers and their configurations Unfortunately the papers containing the fundamental ideas as well as those dealing with experimental molecular structural determinations have been partly overlooked by the chemists publishing papers dealing with the chemistry of *cyclo*hexane and related substances This is indeed one of the reasons for writing the present article

It would, we think, be most useful for the further development in this field if the experimental work on molecular structure could be extended to a considerably greater number of relatively simple substances than those already investigated The results, particularly the variation in energy contents of different stereoisomers, are likely to have considerable value, for instance, in interpreting their chemical properties *e g.* the variations in toxicity of different chlorsubstituted *cyclo*hexane derivatives such as *Gammexane*, used as insecticides

In *Table I* the chief results so far reported about the configurations of simple *cyclo*hexane derivatives, based on x-ray, electron diffraction and in some cases dipole moment measurements, have been listed We have not included the *cyclo*hexandiols in *Table I* because here the direct molecular structure methods have so far been of minor importance for the decision whether a substance is a *cis* or *trans* form

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Recent Advances in Knowledge of Wool Structure

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Wool and the keratins generally are unique among proteins in having a recognizable histological structure which permits the simultaneous investigation of their chemical and physical properties at various structural levels in a way that is often impossible for other proteins Whilst this is very useful from a practical standpoint, it makes a general review of the subject difficult since a clear-cut consideration of different aspects of work on wool is impossible, and furthermore, no completely satisfactory synthesis of the various aspects is possible In the present survey the general plan will be to consider all recent work at various levels of organization, commencing with the molecular level, then the macromolecular and finally the histological level of structure, subdividing each broadly into physical and chemical investigations

FINE MOLECULAR STRUCTURE

The two major physical techniques so far utilized at this level of organization have been wide angle x-ray diffraction and *infra-red spectroscopy* X-Ray diffraction studies have added little to the pioneer observations of W T Astbury and A Street[1] in this field, but there have been many speculations on the nature of the configuration of the peptide chain giving rise to the α fold It seems probable that the most profitable line of approach will be from studies on amino acids and peptides x-ray diffraction patterns closely resembling the α photograph have already been obtained from polypeptides of relatively simple composition[2] Infra-red spectroscopy, and particularly using polarized infra-red, is a technique which has only been applied to problems of protein structure fairly recently, but has already yielded one important result, namely that N–H bonds are essentially parallel to the fibre axis in α-keratin and perpendicular to it in β-keratin[3] This would seem to fit in better with M L. Huggins' suggested structure[4] for α-keratin than many of the alternative suggestions.

Due to the greatly improved methods of amino acid analysis which have been developed recently, the amino acid composition of wool is now known fairly completely within certain limits Thus it is possible to collect figures suggesting that over 98 per cent of the total nitrogen of wool can be accounted for by summing the percentage of each amino acid present It has long been realized, however, that the compositions of different wools may vary considerably in respect of their cystine content, and this variability must necessitate corresponding changes in other amino acids An investigation of these secondary variations would be a most important contribution and could lead to interesting results, but so far has not been attempted

While this problem of variable composition has always been obvious for wool because of its high sulphur content and the ease and accuracy of total sulphur estimations, there are indications that it may in fact be a general problem of protein analysis Thus, recent work by F A Csonka[5] suggests that the composition of crystalline egg albumin can be significantly affected by the hen's diet, and there are other indications in the literature of a similar effect with other proteins *cf e g* the sulphur contents of insulin quoted by G L Miller and V du Vigneaud[6] and M Sahyun[7] It should also be emphasized that the quoted amino acid compositions of wool are really derived from unrelated analyses of different wools

One rather surprising regularity in amino acid composition has been found by R J Block[8] to occur throughout the keratins This is that for all keratins the molecular ratio of arginine : lysine : histidine : 12 : 4 : 1 The unexpected nature of this result is that it is only the ratio which is constant, the actual percentage of arginine for instance can vary quite widely in differing keratins The ratio is not, of course, completely invariable, but viewed against the wide fluctuations in cystine, tyrosine and glutamic and aspartic acids contents expressed in the same way it is nevertheless quite remarkable

Probably the most interesting recent work on wool chemistry however has been the studies on partial hydrolysates of wool by R. CONSDEN, A H GORDON and A J P MARTIN[9], using the techniques of ionophoresis and paper chromatography which were developed by them for this specific problem About forty different dipeptides have been separated and characterized fairly completely from partial hydrolysates of wool, in addition to a large number of other peptides less certainly characterized So far, only the results of an investigation of the acidic peptides[9] have been published in any detail but a preliminary note on the cystine peptides[10] has appeared, whilst it is evident from a recent review by R CONSDEN[11] that some investigation of the basic and neutral peptides has also been carried out The most important result found in the investigation of the acidic fraction has been the frequency with which negatively charged polar residues occur linked together Thus the peptide found in largest amount in this fraction was glutamyl glutamic acid, while serine and tyrosine also occur linked directly to glutamic or aspartic acids On the other hand, there are probably no linkages between two basic amino acids These two results, while not definitely excluding salt linkages of the type envisaged by J B SPEAKMAN and M HIRST[12], would certainly seem to render their occurrence much less probable it is interesting that doubts as to the validity of the salt linkage hypothesis have recently been expressed on other grounds[13] Taken in conjunction with Block's results these findings suggest the possibility of an entirely different distribution of charges over the keratin molecule from that postulated by Speakman and Hirst, namely, a diffuse scattering of positive charges with local concentrations of multiple negative charges on portions of the peptide chains

Whereas therefore on the salt linkage hypothesis the charged groups are envisaged as holding the molecule together solely by the attraction of positively and negatively charged groups, on the above view, forces of repulsion, more especially between positively charged groups, would also play their part in determining the configuration of the peptide chains Repulsion between negatively charged groups would be relatively unimportant because these groups occur directly linked together, and thus negatively charged centres would be well separated spatially It is possible on this view to explain in a qualitative way many of the remarkable setting and supercontraction properties of deaminated and methylated wools for which no satisfactory alternative explanation is available Thus methylation of the fibre, by destroying ionic attractions, would lead to a longer equilibrium length for the peptide chains Conversely deamination of the fibre would leave only forces of repulsion between very widely spaced multiple negative charges, and thus make a shorter equilibrium length more probable

It is also noteworthy that W T ASTBURY's[14] hypothesis of the alternation of polar and non-polar residues along the peptide chain is no longer tenable in view of these results It is interesting too to compare these results with F SANGER's[15] recent work on the terminal amino acids of insulin for which sequences involving glutamyl glutamic and aspartyl glutamic acids have been found

Investigation of the cystine peptides of wool has shown that cystine is linked to most of the other amino acids including glutamic and aspartic acids A considerable fraction of the proline also occurs directly linked to cystine The possible significance of this will be discussed later

In contrast with all the above chemical techniques involving breakdown of the wool, some preliminary investigations on the mode of synthesis of wool fibre have been made using wool roots prepared by the technique of W J ELLIS, J M GILLESPIE and H LINDLEY as the experimental material[16] Although the work is still in its preliminary stages, one or two interesting observations have been made Thus most of the amino acids which are major components of the wool fibre have been detected free in extracts made from wool roots, the two major exceptions being cystine and proline While both these amino acids are difficult to detect in minute amounts it is possible that this finding implies that they may be incorporated into the formed peptide chain by modification of other residues Another result which may be of significance, although also of a somewhat negative character, is the failure to find any large amounts of simple peptides in wool root extract Amino acids are present only in minute amounts (*c* 0 001 μg amino acid nitrogen per wool root) but the amount of simple peptides present seems to be small compared even to this Peptides which have been separated probably contain at least ten amino acid residues with glutamic acid and glycine preponderating One of the major problems of the work, however, is that the precise pattern of amino acids and other metabolites varies from one wool root sample to another for reasons which are not at present understood Some interesting histochemical observations on the mode of formation and hardening of the wool fibre have also been made by E H. MERCER[17].

MACROMOLECULAR STRUCTURE

Although the major chemical advances in our knowledge of wool structure have been made at the molecular level, the most interesting developments in the physical field have been in the studies of the macromolecular structure The reason for this lies in the perfection of the electron microscope which allows direct observation of structures which previously could only be studied by indirect methods The development of small angle x-ray diffraction has also helped to extend our knowledge of macromolecular structure, but this technique, although potentially capable of yielding more information than the electron microscope, is hindered by the difficulty of interpretation of the results

Numerous studies of the electron microscopy of wool have been published, but probably the most extensive are those of E H MERCER, A L G REES *et al*[17] Granting their initial assumption that the products obtained by prolonged tryptic digestion of wool represent genuine structures pre-formed in the fibre and are not artefacts of hydrolysis, there now seems little doubt that the fibrous keratin develops from a corpuscular protein J FARRANT, A L G REES and E H MERCER[18] originally suggested that the non-crystalline matrix material consisted of particles about 100 Å in diameter, in which were embedded fibrils made up of similar particles linearly aggregated after the fashion of a string of beads Mercer has recently concluded, however, that the fundamental unit in the fibrils is larger and this would bring the electron microscope evidence more into line with the x-ray evidence of R S BEAR[19] and I MCARTHUR[20] who find a period of about 200 Å along the fibre axis while still leaving unexplained the failure of x-rays to pick up a 100 Å periodicity It is possible that the size and shape of the particles have been affected by the isolation procedure work at present in progress should throw more light on this

Our knowledge of the nature of the cuticle of the wool fibre has also been greatly extended by recent electron microscope studies and it appears that this is made up of a number of components differing markedly in their resistance to enzymes Most surprising perhaps is the discovery of a continuous membrane associated with the wool cuticle originally thought to be sub-cuticular but recently stated to be epicuticular[21]. If the latter suggestion is correct it provides an explanation of a number of incompletely understood properties of wool, such as the difficulty of wetting clean wool, the difficulty of staining undamaged wool, and the Allwörden reaction The chemical nature of this sheath is unknown, as also is its mode of formation

E. H. MERCER[22] has recently studied the dispersion of wool obtained in urea bisulphite solution and has shown that under suitable conditions, such a dispersion can be drawn into fibres which give a typical α photograph by x-ray diffraction This seems to be the only technique so far known by which a hard keratin after dispersion can still be regenerated in the α form The molecular weight of such a dispersion has also been estimated by E H MERCER and B OLOFSSON[23] to be of the order of 85,000, whereas sodium sulphide and sodium thioglycollate dispersions of wool have molecular weights of about 9,500 From sedimentation and diffusion data they suggest that the 90,000 unit is made up of linear aggregates of the lower molecular weight structures linked together by some bonds which are readily broken by reducing agents under alkaline conditions. They suggest that these may well be disulphide bonds, a suggestion closely analogous to an earlier speculation put forward on other grounds by H LINDLEY and H PHILLIPS[24]

Little chemical work has been done on components at this level of organization, but the results obtained by W B GEIGER[25] and H LINDLEY[26] suggest that here is an interesting potential field of investigation

HISTOLOGICAL STRUCTURE

The interpretation of the elastic properties of the whole fibre in terms of its structure by W T ASTBURY and H J WOODS[27] has led to an enormous amount of work being carried out on the physical properties of fibres before and after chemical modification Two general criticisms may, however, be made of this earlier work First, for convenience of handling, most of the observations have been made either on Cotswold wool or human hair There is now some evidence, however, that some of the properties shown by these fibres are not shared by the much more common merino and cross bred fibres of commerce, and hence cannot be taken as properties of wool in general Secondly, some of the early work suffers from the lack of suitable chemical methods of analysis, so that the nature of the reactions was inferred from model experiments with simple model substances or from known chemical reactions of organic radicals This approach is valuable, but can be very misleading, as has been shown particularly in the reactions of the disulphide bonds of wools Thus there were many early speculations on the nature of the reaction of wool with alkalis, and many reactions based on textbook organic chemistry were put forward It now appears[28], however, that two reactions occur, one in which sulphur is split out completely from the disulphide bond, leaving two combined α-amino-acrylic acid residues in the chains, and the other in which one sulphur atom only is split off, leaving a lanthionine residue[29] Of these two reactions an analogy with simpler substances is only known for the former[30] , the latter seems to occur only in proteins

The fact that two separate reactions occur between the combined cystine of wool and alkali is of some interest and suggests that the reactivity of the cystine is dependent on its location in the wool molecule This idea has received considerable confirmation from a study of other reactions of the wool disulphide bonds Thus by studying the interaction of wool with bisulphite solutions it has been shown that four differing degrees of reactivity of the disulphide bonds can be detected[31] Further work on chemically modified wools has shown that the reactivity of one fraction is probably associated with the presence of four free carboxyl groups in the neighbourhood of the disulphide bond and, by analogy, that another fraction of closely similar reactivity has amide groups in close proximity to the disulphide bond[32] Little is known of the special configurations associated with the other types of cystine reactivity, but there is some evidence to suggest that proline residues may occur near part of the cystine[10] [33] This cystine fraction may well be the serially linked sulphur bonds of Mercer and Olofsson Work with wool reduced by thioglycollic acid has lent further support to the differing reactivity of the combined cystine[33], in particular, reactions involving cross linking the reduced wool have provided valuable evidence of the reality of the differing fractions[34] The interaction of wool and formaldehyde solutions is yet another reaction which has provided valuable confirmatory evidence of these conclusions[35, 36] Some work has also been reported to show that some of these differences extend to non-fibrous proteins in addition to being general reactions of the keratins[37] A general review of this work has already been given by H PHILLIPS[38]

However, in addition to their chemical interest, all these reactions have a special significance for wool, since they can affect the physical properties of the whole fibre to a very considerable extent Thus the reaction of wool with alkalis is of interest from the standpoint of theories of the 'setting' of wool and the permanent waving of hair If a wool fibre is boiled in a mildly alkaline solution while in the extended state it loses its power to contract and is 'set' at its extended length Even boiling the set fibre in water in the absence of tension fails to cause contraction to its original length, although some of the 'set' is lost On the other hand, if the extended fibre is steamed for only two minutes and the tension then released while the steaming is continued, the fibre 'supercontracts' to less than its original length The original explanation of W T ASTBURY and H J WOODS[37] was that these phenomena were due to the simultaneous occurrence of side chain breakdown and linkage rebuilding with the former predominating at short periods and the latter being the determining factor in longer periods of treatment of the fibre J B SPEAKMAN[39] later suggested that the initial breakdown involved was that of disulphide bonds and put forward various suggestions for linkage re-building which later had to be abandoned with the exception of lanthionine cross links which were assumed to be responsible for set S BLACKBURN and H LINDLEY[40] on the basis of reaction rates and other evidence, however, have recently suggested that the nature of setting reactions under these conditions involves low rather than high energy bonds and can thus be regarded as physical rather than chemical Somewhat similar conclusions seem to have been reached by E ELÖD and H ZAHN[41] and P ALEXANDER[42] It is noteworthy that wool which has had its amino groups removed by deamination fails to take a set with alkalis and supercontracts readily, whereas wool which has had its carboxyl groups esterified behaves in precisely the opposite manner i e it sets more readily and supercontracts less than untreated wool If one adopts physical mechanisms for setting and supercontraction, these observations, as has been mentioned previously, throw doubt on the salt linkage hypothesis On the other hand, chemical studies on the reactivity of deaminated and methylated wools suggest no chemical explanation from known chemical reactions[43, 44] However, as discussed earlier, these results can be accounted for qualitatively on the assumption of different distributions of the positive and negative charges over the protein chains

Supercontraction can also be brought about by boiling wool fibres in sodium bisulphite solution—indeed it was this observation which first led Speakman to postulate that the initial side chain breakdown occurring under the Astbury and Woods condition of supercontraction was disulphide bond breakdown. A very full investigation of the relation between the physical properties of bisulphited wool and the chemical reactions involved has been carried out by E G H CARTER, W R MIDDLEBROOK and H PHILLIPS[45] They showed that the changes in elastic properties and ability to supercontract could be related to the particular cystine fraction involved Whilst, here, there is no doubt that supercontraction is accompanied by disulphide bond breakdown, the authors point out that this alone is insufficient The fibre must also be subjected to thermal agitation before contraction occurs, and therefore the breaking of hydrogen bonds is probably also necessary for supercontraction. Another interesting result was the finding that rupture of half the cystine linkages of the wool has less effect on the elastic properties of wool than solutions of monochloracetic acid, which presumably exerts its effect by interfering with ionic attractions and possibly hydrogen bonds Some interesting studies on the effect of reduction and reformation of sulphur cross links in wool have been carried out by M Harris and A. E Brown[46]

In recent physical studies of the elastic properties of wool fibres emphasis has been placed on the separation of entropy and internal energy effects This is not a simple matter, but both H B Bull[47] and H J Woods[48] have concluded that entropy decreases with extension for extensions up to 20 per cent This conclusion has recently been challenged by K H Meyer and B Haselbach[49] The alternative explanation they put forward is not, however, at present supported by any experimental evidence The experiments quoted are inconclusive, as has been pointed out by H J Woods[50] Interest is also being shown in other elastic properties of wool apart from the more studied Young's modulus and torsional modulus A B D Cassie[51] has recently advanced a suggestion to account for the warm feeling of wool as opposed to the chilliness of silk or cellulose fibres based on the unusual bulk elastic properties of wool

CONCLUSION

As is obvious our knowledge of wool structure is very incomplete , indeed, it would be true to say that the past decade in wool research has served mainly to show the complexity of the problem Despite these immediate difficulties, however, there does seem to be the possibility of major discoveries in the near future X-Ray crystallography of amino acid polymers suggests that the precise nature of the α fold may not elude us much longer and the problems of amino acid arrangement in proteins seem at long last to be yielding F Sanger has now accounted for something like a quarter of the insulin molecule in penta- and tetrapeptide sequences The major problem that awaits solution in the field of wool structure is the separation of the fibre into its component structures This is a problem which has grown steadily in complexity with the realization of the heterogeneous nature of the wool fibre, and it is here that studies of the wool root may assist by providing us with a more tractable starting material Perhaps we may even hope that studies on the wool root will lead to the discovery of a vital clue to the most intractable problem facing biochemistry today —the mechanism of protein synthesis in the living cell

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The Road Research Laboratory of the D.S.I.R.

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Director of Research

THE road transport industry is one of the biggest of Britain's industries The services it provides cost some thousand million pounds a year and about one and a quarter million persons are engaged in making, repairing, servicing, and driving road vehicles and in maintaining the road system Road accidents have been estimated to cause an economic loss to the country of some £100,000,000 every year In addition every active member of the community is a road user, as a pedestrian, as a cyclist, as a motorist or as a user of road vehicles, and has a direct and personal interest in the efficiency of the roads There is, therefore, a wide field for road research

Road research began as a recognized activity of the Department of Scientific and Industrial Research in 1933, when a small experimental station, set up some years earlier by the Ministry of Transport on the Colnbrook By-pass, was taken over together with its staff as a beginning to the close collaboration with the Ministry which has been an essential feature of the Laboratory's work At first the research was largely concerned with road materials and methods of road construction but after the 1939 war its scope was broadened to include problems of road layout, traffic and safety

In the public mind research is the job of a class of men who live and work apart This conception is wrong for most kinds of applied research it is particularly wrong for road research Road research is essentially a joint affair, the business both of those responsible for the country's roads and of the engineers, physicists, chemists, mathematicians and others who form the complement of the Road Research Laboratory The task of the Laboratory is to discover ways of improving the roads of Great Britain by making them better able to carry the traffic and safer to use, and to do so at a reasonable cost At the present time the cost must be stressed research must be directed to obtain the greatest return in the quality and safety of our roads for the very limited amount of money that is available

On the materials side the main investigations are, broadly speaking, conducted in three stages *1* the work that must be done under the carefully controlled conditions of the laboratory, *2* the semi-full scale stage involving experiments to test laboratory findings under conditions met with in practice, and *3* the full scale trial These three stages lead finally to the drafting of specifications and to their adoption, where proved successful, by the highway authorities

On the safety and traffic side the procedure may sometimes be the same Since the data required by the scientists are more often than not obtainable from the behaviour of the road user and from accident and traffic statistics, the laboratory work is largely concerned with the development of measuring instruments for use on the roads of the country and with the collection and analysis of results In a sense, for safety and traffic studies, the highways are also the laboratory

The grouping of the Laboratory's work in two divisions forms a convenient way of summarizing the investigations now in progress investigations on road materials and construction, and investigations on road safety and traffic flow problems

INVESTIGATIONS ON ROAD MATERIALS AND CONSTRUCTION

On the 'materials' side the technical problems are fundamentally simple Some 5,000 tons (5,080 tonnes) of material are required to provide a surfacing 6 in (15 2 cm) thick on a road a mile (1 6 km) long and 30 ft (9 m) wide This limits the choice of roadmaking materials to those which are plentiful, widespread and cheap, such as mixtures of sand and broken stone or other 'aggregates' held together by some relatively cheap binder such as bitumen, tar or Portland cement If locally occurring materials can be used economies in transport are realized

The problems are thus largely those of developing sure methods of selecting the best materials for given conditions and of combining and using them in the best way The whole field is a large one but certain parts of it can profitably be surveyed as an indication of the methods of attack

Pavement design— An earth-track by itself is unsuitable for modern traffic the soil will not bear the weight of the traffic and is abraded away It must be covered by a hard durable surfacing sufficiently thick to spread the loads provided by the traffic until they are less than those that the soil will safely bear Many ways have been devised in which the minimum thickness needed for a road surfacing may be calculated from a knowledge of some property or combination of properties of the underlying soil, from assumptions regarding the nature of the surfacings and from an estimate of the likely traffic loads. Unfortunately these calculations give different answers according to the initial assumptions made

What is required, both to select the most promising theories and to improve upon them, is the determination of this minimum thickness for a number of surfacing materials carrying different weights of traffic on each of a number of different types of soil The methods of calculation and the assumptions made must be checked under practical conditions This involves building roads The first material selected for study was concrete It has the advantage that for many mathematical calculations it can be assumed to behave like an elastic solid The opportunity for the first of these full scale experiments was provided in 1946 during the construction of a dual carriageway on road *B 688* at Oxton in Nottinghamshire where a preliminary soil survey had shown the subgrade to be a gravel-sand very uniform in its properties over considerable stretches of the proposed road In this experiment, slabs of different thicknesses, both plain and reinforced, have been laid on the subgrade itself and on various thicknesses of sand-cement base , some of the slabs are thinner than would normally be put down to make sure of determining this minimum thickness with some precision The further objects of the experiment were to find the minimum thickness of concrete to be associated with each different thickness of sand-cement base and to link this information with seasonal measurements of slab deflection under known loads and under traffic, and with mechanical tests and other measurements on the subsoil

Other similar experiments will be made as opportunities permit Where the construction of a new road has been agreed to, the additional cost of making it an experiment is small and the long term economies resulting from the information to be gained may be large

Soil studies— In the investigation just described the soil is treated as an engineering material Ancillary investigations are in hand to develop methods of assessing the relative value of different soils as supporting media for a road surfacing , basically these methods involve applying various types of loading to the soil and measuring the movements produced

Soil as an engineering material is unique in two respects its bearing power is improved very greatly by compaction and its mechanical properties are largely controlled by the amount of moisture it contains These properties of soil have made it necessary to carry out two other lengthy investigations The first comprises a study of the changes in the mechanical properties of different types of soil produced by compacting them, using all kinds of compacting machinery over a wide range of moisture contents The information thus obtained is combined with methods of classifying any new soil met with into one or other of the types studied A great deal of such information has been collected over the last few years, providing a general guide to the type of equipment to be used and to the methods of using it

The second group of investigations is designed to supplement this work it comprises studies of the laws of the movements of moisture in soils so that the moisture content of the soil under a proposed new road may be predicted from the soil type and from measurements of the depth of the water table These investigations are still at an early stage but evidence is being obtained which suggests that after a road has been constructed the moisture content of the soil foundation tends to some mean value governed by the local conditions which may be thought of as an ' equilibrium ' moisture content It is thus possible to use this concept of a predicted ' equilibrium ' moisture content to plan both the treatment of the soil in constructing a new road and the ' design ' of the surfacing to be put on it The soil is then compacted at or near this ' equilibrium ' moisture content, thus reducing to a minimum any shrinkage or swelling of the soil arising from changes in its moisture content during the life of the road

Machinery researches— The man with wheelbarrow and shovel is or should be obsolete on the roads of Great Britain , manpower is being reduced wherever possible by the increasing use of machinery Now that economic conditions have compelled the suspension of schemes for new roads and the major reconstruction of old ones, the improvement of machinery used in road maintenance is one of the Laboratory's main preoccupations

Statistics show that out of the 180,000 miles of road in Great Britain 100,000 miles are maintained by ' surface dressing ', that is by spraying the road with tar or bitumen to keep it waterproof and then scattering stone chippings on the fresh binder to keep the road non-skid To improve the overall efficiency each of these processes had to be tackled quite differently The binder is sprayed by a relatively complicated machine operated by only two men whereas the chippings require a large number of men to spread them To hold the chips in position they must be packed on the road shoulder to shoulder, with the binder rising up in the channels between the stones until it is nearly touching their top surfaces , in this way each stone is held to the road and to its neighbours on all sides The actual amount of binder to be put down is controlled by the size of the stone to be used and other factors, but the sprayer must be capable of putting down this amount and in a uniform film On the other hand, within wide limits the rate of spread of the chippings has little effect on the quality of the final work but they are expensive to buy and spread.

Improvement in the technique of spreading the binder had of necessity to be achieved by the better use of existing machines since the wholesale production of new machines was an impossibility This improvement was realized by developing simple tests for measuring the thickness and uniformity of the binder film and by encouraging machine operators to fit special low speed speedometers so that they might know what they were doing more easily The savings made by this kind of work are not small On the average a surface dressing lasts five years whereas some dressings have been down twelve years or more if the average life could be increased to seven years the saving in a large county would be some £40,000

A survey of commercial work in spreading chippings showed seven men spreading at the rate of 166 sq yd per man hour on one job while on another nineteen men achieved only 50 sq yd per man hour With careful planning and the best type of machinery it was found that eleven men could spread 2,500 sq yd per hour without fatigue *i e* 230 sq yd per man hour These facts have been brought to the notice of local authorities and the interest awakened has led to reductions in the labour costs of surface dressing

Another group of investigations dealing with machinery is concerned with concrete mixers, with machinery for placing the freshly mixed concrete on the soil foundation and with vibrating machinery for compacting and finishing the concrete road slabs Here the problems arise from the fact that the more water is added to the concrete in mixing the easier it is to place and work to a flat finish, but the weaker it is when set reducing the water too much, on the other hand, makes the concrete stick in the mixer and renders it troublesome to place and finish The task of the research worker is thus to study the working of each type of machine in detail, making modifications in the machines or their mode of use where desirable, so that drier concretes may be used satisfactorily

INVESTIGATIONS ON ROAD SAFETY AND TRAFFIC FLOW PROBLEMS

In 1946 the terms of reference of the Road Research Board were widened to permit work on road safety as a specific object of research Before 1946 the work on road surfaces touched on road safety only in so far as one of the desirable qualities of a road surface is its freedom from liability to cause skidding in wet weather. For purposes of classification, the road safety researches are divided into three groups concerned respectively with road, vehicle and road user.

The first group visualizes the road network of a district as a service to the people living there, part of their apparatus of living. The first thing to find out is how this road network functions and how it is used This involves taking censuses of traffic, measuring journey times and traffic speeds—finding out the amount and type of traffic using each road and the effectiveness with which each part of the network handles the traffic through it A good deal of work has been put into this subject already, largely in devising and developing the tools needed, traffic counters, speed measuring apparatus, air photography and other devices for recording traffic behaviour

An allied investigation concerns road intersections and roundabouts, this is being carried out on a disused airfield where various types of road intersection or roundabout can easily be improvised, these are fed in various ways with numerous vehicles in succession providing the 'traffic' This procedure gives a measure of the handling power of each type of intersection

Investigations concerned with the vehicle deal with brakes and brake testing, controllability, visibility from the driving seat, night driving problems, including dazzle, together with other problems concerned with vehicle lights The police are, and have been, collaborating with the Laboratory to the great advantage of the work in the investigations relating to headlight dazzle and to the relation of brake efficiency to accidents The investigations concerned with the road user are carried on jointly with the Medical Research Council they deal with driving habits, fatigue, accident proneness and the like

The collection and interpretation of statistics are vital to the conduct of road safety research There is a large number of data required concerning all types of road accidents, and the statistics group of the Laboratory is collaborating with the Ministry of Transport, the Home Office and the Police Many local authorities are also providing statistical material for this work, for example, they are collaborating in obtaining records of accidents at particular types of intersection with a view to developing improved types

Of all these many investigations two of general interest and importance will be mentioned, they are concerned respectively with the problem of dazzle and with pedestrian crossings

Dazzle— Records of Army service vehicles showed that dazzle was recorded as having been a contributory factor in one out of every eight night time accidents

The first investigation undertaken was of the existing practices of the road user With the help of the police observations on some 11,000 vehicles were made at night on important traffic routes. It was found that only a small proportion of drivers did not dip or switch to a passing system for an approaching vehicle only 1 in 20 for unlighted roads and 1 in 50 for lighted roads. Yet there was a high proportion of vehicles with dazzling lamps 1 in 4 on unlighted roads and 1 in 10 on lighted roads. For every hundred cases of dazzle on unlighted roads 38 were caused by dipped headlamps, 37 were caused by passlamps, and 25 were caused by undipped headlamps. Most of the dazzle arose not from any failure on the part of motorists to switch to dipped or passing systems, but to faults in these systems.

Further analysis showed that although passlamps were responsible for nearly as many cases of dazzle as dipped headlamps they were not nearly so common on the road. No less than forty per cent of all passlamps were dazzling, compared with seventeen per cent for dipped headlamps. The passlamp has thus by far the worst record of all types. This was attributed to misalignment, for the setting of such a lamp is very critical. The lower the lamp is mounted the more nearly horizontal it must be set for a given visibility distance.

As a result, a regulation was issued by the Ministry of Transport which came into force on 1 January 1949 prohibiting the use of passlamps mounted less than 2 ft above the ground.

The recommendations made by the Road Research Board[1] as a result of this work also contained detailed instructions for adjusting headlamps. It was felt that the motorist should be told not only the correct alignment of the lamps, but also the methods of making such alignments.

Pedestrian crossings—Pedestrian crossings are intended to reduce road accidents by organizing the movement of pedestrians across the street. The first question that arises is whether the present methods of marking the crossings are satisfactory or whether they could be improved upon.

The Ministry of Transport felt that Belisha beacons and studs could usefully be supplemented by some kind of surface markings on the strip used by the pedestrian, and the Laboratory made estimates of the relative visibility of different types of pattern using a model street. They found that wide alternate black and white stripes parallel to the kerb were the most visible form of marking from the position of the approaching car driver. As the next step, five hundred marked crossings were laid and five hundred crossings at comparable sites were selected for parallel observations of the behaviour of both pedestrians and motorists. It was hoped that this number would be sufficiently great to permit any large differences in accidents to be detected.

In addition, fifty crossings were chosen, twenty five marked and twenty five unmarked, for intensive observation of the behaviour of pedestrians and drivers. The crossings were marked just before the Ministry of Transport's Pedestrian Crossing Week in April 1949, and so with the marked crossings the effects of marking and propaganda reinforced each other. *Figure 1* shows the great improvement in behaviour of pedestrians plotted against time for men, women and children. The broken line in the diagram refers to the crossings where both marking and propaganda were applied. It will be seen that the effect of marking plus propaganda is in both cases greater than the effect of propaganda alone, that the improvements in behaviour lasted more than nine months, and that the residual effect of marking after this period is as great as the temporary improvement from the propaganda alone. This investigation is still proceeding.

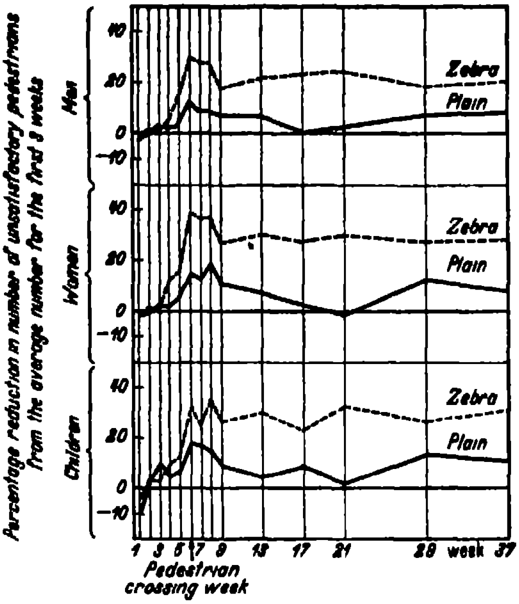

Figure 1 *Record of behaviour of pedestrians*

PUBLICATIONS AND PUBLICITY

When a particular investigation is concluded the Laboratory's task is only half done, the results obtained must be brought to the notice of the 'user' in a palatable form. The Laboratory relies on its publications to accomplish some of this task—these comprise *Road Notes* consisting of summaries or recommendations intended for immediate practical use, *Technical Papers* describing at a greater length particular researches or fields of knowledge, the Annual Report and articles and papers to learned societies

It is the constant aim, however, to develop between research worker and 'user' public relations of a more personal nature. In so large a field of activity this presents a problem of special difficulty but it is being attacked in several ways Thus full scale investigations are conducted in many parts of the country, visits of our staff to inspect failures and discuss problems are arranged, and visits to the Laboratory of engineers and other executives are welcomed In addition lecture courses for practising road engineers are organized at the Laboratory, providing instruction in the theory and practice of advanced techniques in soil engineering, in concrete and bituminous road construction In these and other ways we seek to encourage the free interchange of information and opinion between the 'user' and the research worker at all levels

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Miscellaneous Notes

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

Road Research Laboratory—Tests have been carried out on the visibility of motor cars in daylight fogs, using a dark coloured car which, without lights, was just visible at 100 ft Sidelights made little difference but a headlight with a low intensity of 2,000 cp could be seen at 200 ft Raising the intensity to 60,000 cp increased the visibility to 300 ft Medium sized headlamps fitted with 36 watt bulbs emit a beam with a forward intensity of about 20,000 to 30,000 cp from each lamp, this can be seen at about 250 ft *i e* at about two and a half times the visible distance of the unlighted vehicle The risk of dazzle is negligible in daytime

RESEARCH ASSOCIATION

British Welding Research Association—The Association has published a booklet on the photographic aspects of the radiography of welded high pressure vessels The publication reviews the desirable characteristics of the sensitive photographic materials used, outlines the theoretical and practical reasons for the choice of a material in a particular case, gives recommendations for the handling and processing of the films and enumerates the defects which may arise

NATIONAL RESEARCH COUNCIL, CANADA

River model—A scale model of the entire Fraser river delta has been put into operation a few miles away from the 'original' The main purpose of the model, which covers an area of 900 × 400 ft, is to study proposed channel improvements between the ocean and a port about 25 miles upstream Local problems of channel maintenance will be considered and the model will also serve as a source of general information about tidal rivers which carry large quantities of silt

The model is supplied with water by a pump from a reinforced concrete reservoir, water level is controlled by a set of tilting weirs which return the water to the reservoir The weirs are hydraulically operated and are controlled by an 'electronic eye' which follows the tide curve drawn on a transparent chart Tide control and river discharge control are synchronized and are so designed that without attention they duplicate the actual tide and river levels over a period of a whole year

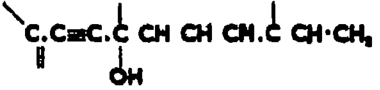
Electrostatic accelerator—An accelerator capable of producing at least four million volts has been put into operation at the Chalk River atomic energy plant It is utilized as a source of high speed atomic beams for breaking up atomic nuclei and will serve as supplementary equipment to the atomic pile The machine, which weighs fourteen tons, can be used to accelerate several types of charged particles, including tritium, the third isotope of hydrogen, which is made in the pile

ANIMAL RESEARCH IN FIJI

Experiments in breeding cattle for heat tolerance as well as for high productivity are to be carried out on animals already 'resident' in Fiji The heat tolerance of an animal remains approximately the same throughout its life, and it is planned to make measurements on young cattle in the country of their origin under artificial tropical conditions

CORRECTION

Formula *XXX* on p 460 should read .



$$\diagdown C.C{\equiv}C.\underset{OH}{\overset{Me}{C}}\,CH\,CH\,CH.\overset{Me}{C}\,CH{\cdot}CH_3$$

New Books

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New York and London Interscience Publishers Inc , 1949
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THIS volume presents in book form a series of seven lectures devoted to the discussion of advances made in recent years in various provinces of analytical chemistry The authors are experts in the fields they have chosen, and they discuss the practical use and range of applications of the methods selected, but at the same time in each chapter the subject is introduced by a general fundamental explanation which will enable any scientific reader to understand what follows

In the first chapter I M KOLTHOFF gives an account of the theory and practice of polarography and then discusses amperometric titrations using either the dropping mercury electrode or a rotating platinum electrode, applicable to the determination of concentrations of 10^{-4}N with a precision of ± 0 5 per cent

The next two lectures by J H YOE deal with the uses of organic reagents in inorganic analysis A general discussion is given of the procedure in investigating and establishing a new analytical reagent for a metal and several examples are described from the lecturer's own publications colorimetric reagents for palladium, iron and titanium and a gravimetric reagent for tungsten.

A chapter on infra-red spectroscopy by O A BEECK describes the apparatus and methods used with special reference to the analysis of hydrocarbon mixtures

An excellent account by J HILLIER of the underlying principles and the development of the electron microscope is followed by a discussion of detailed experimental methods in mounting specimens and making observations The chapter concludes with a section on electron diffraction by very minute specimens which shows promise of developing into an important microanalytical method

F. D. ROSSINI's lecture is concerned with the purification and analysis of hydrocarbons. Distillation and chromatographic methods are described and precise analyses by accurate freezing point observations. In the final lecture by J A HIPPLE on mass spectrometry a lucid introduction to the subject is followed by a discussion in some detail of its application to the analysis of hydrocarbon vapours.

The book is as excellently produced and illustrated as is usual with current American scientific works and it can be strongly recommended to anyone looking for an account of recent developments in analytical technique with indications of future trends

G M BENNETT

Metal Rectifiers

H K HENISCH

(*xii+156 pp, 55 illus, 8½ in by 5½ in*)

Oxford The Clarendon Press, 1949 15*s* net

METAL rectifiers have been of great practical importance for at least twenty years, but their development has been largely empirical with, generally, little guidance from fundamental theory. When account is taken of various second order properties, such as hysteresis and creep, the magnitude of which may determine whether a rectifier is suitable for a given purpose, it is evident that the phenomena involved in the conduction of electricity through such rectifiers are by no means simple Sufficient progress in the theory of the solid state has been made in recent years, however, for theory and practice to be linked more closely together for the benefit of the manufacturer and user on the one hand and the physicist interested in fundamentals on the other

In this, the second volume in the series of monographs on the Physics and Chemistry of Materials, the physics of barrier layer rectification in so far as it is understood today is summarized for the practical worker and the newcomer to the subject The book fulfils a definite need It gives a clear account, without detailed mathematical derivations, of the current theories, due principally to MOTT and to SCHOTTKY, together with the relevant experimental data There are concise but interesting chapters on methods of manufacture, earlier theories, rectifier operation and some notes on future development *e g* the use of titanium dioxide There are very few ambiguities or misprints, and the diagrams are good Those working in the field who had the benefit of using the author's bibliography, prepared while he was at the R A E Farnborough, will be glad to see a revised version at the end of the book In a future edition, it would help, however, to add initials to the names of the authors

A brief subject index is provided The book is excellently printed and produced It may be recommended to all engineers and physicists who wish to learn the present position without having to delve into original papers or to sort out a mass of detail, and it will be useful to honours physics students and those who are contemplating working on the subject

F. A VICK

RESEARCH SUPPLEMENT

Transition between Laminar and Turbulent Flow in Various Liquids

G RAUMANN, B Sc, I S NIXON, B Sc and K G DENBIGH, M A, Ph D

Experimental studies have been carried out on the transition between laminar and turbulent flow in the following liquids water, acetone, butanol, ether and solutions of benzopurpurin and polymethyl methacrylate Most of the work was carried out at 20°C, but experiments on ether were conducted also at 0°C and − 80°C The results confirm the correctness of the Reynolds number in determining the stable type of flow, and it seems therefore that the viscosity and the density are the only properties of the fluid which are of significance with regard to the mechanism of the fully developed turbulent motion On the other hand, it has been noted that there are certain specific differences of behaviour between the various liquids regarding the ease of transition between laminar and turbulent flow The presence of colloidal particles, in particular, seems to facilitate the transition It is also shown that the pressure drop in a straight tube continues to be proportional to the fluid velocity in the quasi-turbulent region between Reynolds numbers of 2,200 and 5,000 Above $R_e = 5{,}000$ the present results are in agreement with the equation of BLASIUS

WHEN a fluid passes through a straight channel such as a pipe it is well known that above a certain velocity the character of the motion changes rather suddenly and the flow is said to become turbulent In newtonian fluids, the theory of the fluid motion at velocities lower than the critical value presents no great difficulty and the pressure drop is expressible in the form of Poiseuille's equation On the other hand, the causes of the transition to turbulence are very imperfectly understood, and so also is the quantitative treatment of the turbulent motion itself Certain aspects of this phenomenon are discussed in this paper

As a result of the work of REYNOLDS[1], STANTON and PANNELL[2] and others, it has been found that the occurrence of turbulent flow depends on the value of a dimensionless quantity, the Reynolds number For a circular pipe this is defined as $vd\varrho/\eta$, where v is the linear velocity, d the tube diameter, ϱ and η the density and viscosity of the fluid respectively If the pressure drop in the tube is plotted as a function of this quantity it is found that the curves corresponding to laminar and turbulent flow intersect at a Reynolds number of about 2,200 For the present purposes this point of intersection will be taken as the critical value Turbulent flow does not occur below this value, provided that the tube is straight and the flow is being studied at a point sufficiently far along its length for the eddies created at the entrance to have died out On the other hand it is possible for laminar motion to persist in a kind of metastable state at Reynolds numbers greatly in excess of 2,200, especially when there is an absence of any disturbances to the flow

The Reynolds number as a criterion of turbulence implies that the viscosity and density are the only properties of the fluid which are of significance in the mechanism of turbulence It is therefore rather surprising that there has been very little systematic study of the transition except for air and water, which were the subject of the classical researches of REYNOLDS[1] and others[2] [4] It has seemed worth while, therefore, to make measurements on a number of other fluids of varying degrees of complexity This has been the principal object of our work We have also sought to determine whether temperature has any effect on the critical Reynolds number, apart from its effect on viscosity and density Finally, we have examined the flow of water in a non-wetted tube (polythene) in order to determine any effect of the surface forces

The transition may be investigated by a number of methods, as for example the colour band technique originally used by REYNOLDS and recently greatly improved by BOWEN and BINNIE[5] For our own purpose we chose the second of the methods used by REYNOLDS, namely *the measurement of the difference* in pressure between two points along the tube, at various rates of flow The results on some pure organic liquids and colloidal solutions are in agreement with the view that the Reynolds number is a sufficient criterion of the stable type of flow On the other hand, the various liquids show certain specific differences with regard to the ease of the transition

EXPERIMENTAL

The main series of experiments was carried out on the apparatus shown in *Figure 1*

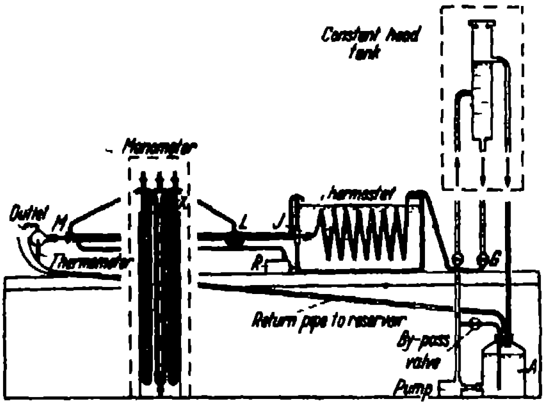


Figure 1 *Arrangement of apparatus*

The liquid under investigation entered the apparatus from a constant head tank which was at a height of 36 ft (11 m) above the laboratory From the tank the liquid descended to a coil contained in a thermostat controlled at 20°C The liquid then entered the experimental tube *JLM* and from its outlet was pumped up once again to the head tank The flow rate was determined by the use of a measuring cylinder and stopwatch The experimental tube consisted of a 0·5 cm precision bore steel tube which was copper lined to prevent corrosion The part of the tube over which the pressure drop was measured was 200 cm in length The portion *JL* preceding the upstream pressure point was detachable and could be varied in length from 42 to 180 pipe diameters This portion will be referred to as the inlet length The whole of the experimental tube, including the inlet length, was jacketed by another pipe in which water from the thermostat was circulated by the pump *R*

The details of the pressure point design, which was based on the one used by GRINDLEY and GIBSON[4], are shown in *Figure 2* This design was chosen as giving the least disturbance to flow The method was to cut the experimental tube and to separate the two parts by a gap of about 0·125 mm This narrow channel communicated with a wider annulus which in turn transmitted the pressure by means of two small holes to the manometer The latter is shown in the inset of *Figure 1*, at small rates of flow the tap *X* was held open and the pressure was measured as a difference in level of the same liquid that was flowing through the experimental tube, at higher rates of flow the tap was closed and the pressure was read from the mercury levels in the central U-tube. The heights of the menisci were measured by means of a cathetometer

The liquids used in the investigation were as follows

a distilled water, for the purpose of comparing results with those obtained by the earlier workers

b acetone

c butanol

d a solution in acetone of 6 per cent by weight of polymethyl methacrylate (average m wt 100,000)

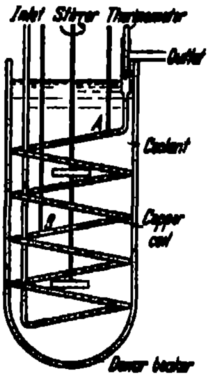
e solutions in distilled water of 0·05 and 0·25 per cent by weight of benzopurpurin 4B

f a solution of 0·005 per cent of benzopurpurin in 0·8 per cent aqueous sodium sulphate solution

The purpose of using the benzopurpurin solution was to investigate the possible effect on the onset of turbulence of the highly anisotropic rod-shaped particles which are known to be present in colloidal solutions of the dye[11] The sol was prepared by adding a small amount of water to the weighed out solid dye and grinding this mixture until a smooth paste was obtained This was then added quantitatively to boiling water and made up to the required concentration After standing for twenty four hours the sols showed a well marked birefringence when examined between crossed polaroids The sols were not used in the experimental apparatus until they had aged for several days in order to obtain constant properties

The viscosities of the various liquids were determined as follows the viscosity of water at 20·0°C was taken as 0·010 poise and, using this figure, the mean diameter of the experimental tube was calculated by applying Poiseuille's law to the measured pressure drop of water in laminar flow This figure agreed very closely with direct measurement Using this value for the diameter, the viscosity of the remaining liquids was then computed by again applying Poiseuille's law to the measured pressure drop of these fluids in laminar flow

In addition to the main series of experiments, as described above, work was also carried out on the flow of water through a polythene tube and on the possible effect of low temperatures on the onset of turbulence The first of these was carried out in an apparatus similar to that already described, in which the copper-lined steel tube was replaced by a polythene tube of fairly uniform bore The low temperature work was carried out on a rather different apparatus, in which a coil was used in place of a straight tube in order that the apparatus could be conveniently immersed in a large Dewar beaker The apparatus is shown diagrammatically in *Figure 3* The coil, which was made of 3·18 mm bore copper pipe, had a diameter of 18 cm, and the pressure drop was measured between two points *A* and *B*, which were 2 m apart along the coil, 2·5 m of pipe preceded



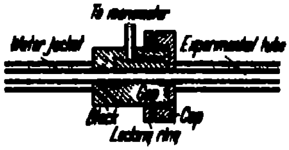


Figure 2 Arrangement of pressure points

Figure 3 Arrangement of low temperature apparatus

the first pressure point in order to attain a steady temperature in the liquid flowing through the coil

REPRESENTATION OF RESULTS

For lack of an adequate physical theory, the quantitative treatment of experimental results on turbulent flow is usually carried out by the method of dimensional analysis For this purpose it is supposed that the only variables which are of importance are the following *1* the pressure difference per unit length of tube, $\Delta p/l$, *2* the linear velocity of flow, v, *3* the tube diameter, d, *4* the density, ϱ, of the fluid, and *5* its viscosity η (If entrance effects are present or if the pipe is rough, additional variables must be included)

Between these five variables an infinite set of dimensionless groups can be constructed, but of these only two are independent, the remainder being products or quotients The two independent groups can, of course, be chosen at will For one of these the Reynolds number

$$R_e = vd\varrho/\eta \tag{1}$$

is universally chosen and is regarded as having a certain physical significance as representing the ratio of the inertial to the viscous forces For the second independent group, the quantity

$$(\Delta p/l) \times (d/\varrho v^2)$$

is often chosen In engineering practice one half of this quantity is frequently used and is called the Fanning friction factor This last dimensionless group is useful in practical work, but it has the disadvantage that the velocity of flow is contained in it, as well as in the Reynolds number, thus obscuring the physical significance of the resultant plot For our own purposes we prefer to multiply this quantity by the square of the Reynolds number This gives a dimensionless group not containing the velocity, which we shall call the pressure factor, P, where

$$P = (\Delta p/l) \times (d^3\varrho/\eta^2) \tag{2}$$

Experimental results can be expressed very conveniently by plotting the value of this quantity against the value of the Reynolds number This is the same procedure as used originally by Reynolds It has the advantage, as compared to the more customary use of the friction factor, that for a particular fluid and a tube of fixed diameter it is equivalent to plotting the pressure drop (or work per unit volume of fluid) against the flow velocity The resultant plot shows very clearly the additional energy dissipation which occurs when the flow becomes turbulent

DISCUSSION OF RESULTS

The results obtained in the main series of experiments at 20°C are shown in *Figure 4* where the experimental values of the pressure factor P have been plotted logarithmically against the Reynolds number for all the liquids under test At a given value of the Reynolds number, except in the unstable transition region, each liquid has the same value of the pressure factor This result confirms the traditional view that the viscosity and density of the fluid are the only properties which are significant in determining the stable type of flow

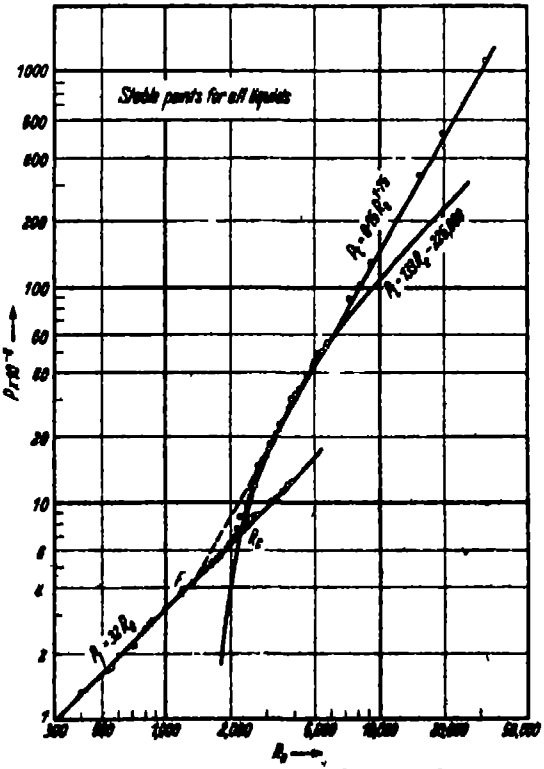


Figure 4 Logarithmic plot of pressure factor against Reynolds number; stable points of all liquids

The more detailed discussion of the results and, in particular, the question whether the above conclusion is also valid in the transition region, can best be carried through by separate consideration of the various types of flow.

Laminar flow—At low flow rates all the liquids including the polymer and dye solutions gave a pressure drop proportional to the velocity, in agreement with Poiseuille's law. Although dye sols frequently show deviations from this law at low flow rates[5], no such deviations were observed on the benzopurpurin sol at the concentrations in use.

The pressure drop in laminar flow according to Poiseuille's law is given by the equation

$$\Delta p/l = 32v\eta/d^2$$

Multiplying through by $d^3\varrho/\eta^2$ gives

$$(\Delta p/l) \times (d^3\varrho/\eta^2) = 32vd\varrho/\eta$$

or

$$P_l = 32R_e \qquad (3)$$

where P_l denotes the value of the pressure factor in laminar flow. In this type of flow the pressure factor is thus equal to 32 times the Reynolds number.

Fully developed turbulent flow—At Reynolds numbers above 5,000 under turbulent flow conditions the pressure drop varies as a higher power of the velocity than in laminar flow. REYNOLDS obtained the exponent as 1·723, but a more frequently used expression is that of BLASIUS[6], according to whom the exponent is 1·75. (At very high Reynolds numbers or in rough pipes it is known[7] that the exponent on the Reynolds number approaches 2.)

The Blasius equation may be rearranged in terms of our pressure factor, as follows

$$P_t = K R_e^{1\cdot75} \qquad (4)$$

where P_t denotes the value of P in turbulent flow and K is a proportionality constant. Our own results at Reynolds numbers above 5,000 are in good agreement with this equation. The mean value of K is 0·15, which is not significantly different from the value $K = 0·158$ obtained by BLASIUS.

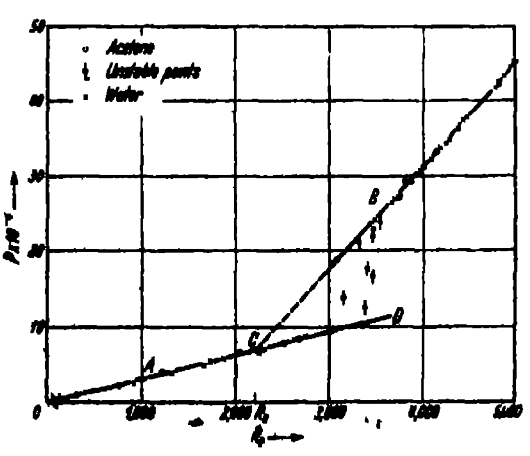


Figure 5 *Pressure factor plotted against Reynolds number for acetone and water*

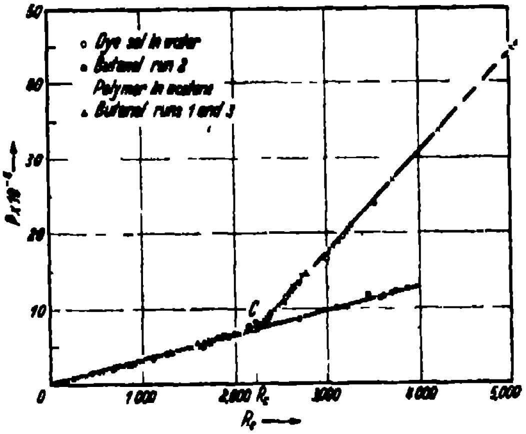


Figure 6 *Pressure factor plotted against Reynolds number for butanol and sols*

The region 2,000 < R_e < 5,000—The intersection of the curves defined by equations 3 and 4 (when $K = 0·15$) is shown at F in *Figure 4* and occurs at a Reynolds number of about 1,300. This point has no clear significance because equation 4 ceases to give good representation of the results at Reynolds numbers below about 5,000. Below this figure the experimental curve passes imperceptibly into a straight line such that the pressure drop is directly proportional to the velocity, and not to the 1·75 power of the velocity as in the fully developed turbulent flow. This is shown more clearly in *Figures 5* and *6* where the experimental results on the various liquids at Reynolds numbers below 5,000 are shown on a larger scale than in *Figure 4*. It is to be noted that whereas *Figure 4* is a logarithmic plot, *Figures 5* and *6* are direct plots of P against R_e.

The straight line which represents the turbulent or quasi-turbulent flow at Reynolds numbers below 5,000 intersects the line (equation 3) which is representative of laminar flow at an angle. The point of intersection, for all the liquids examined by us, occurs at a Reynolds number of about 2,200, and it is this point which we described at the outset as the critical point of transition. This point is represented in *Figure 4* at R_c, and in *Figures 5* and *6* at C.

The quasi-turbulent flow below $R_e = 5,000$ can thus be represented approximately by a linear equation as follows

$$P_t = 133\,R_e - 225{,}000 \qquad \ldots (5)$$

where P_t denotes the value of the pressure factor in this intermediate region Equations 3 and 5 give identical values of P at $R = 2{,}200$, the critical point On the other hand, this is not necessarily the actual point of transition This distinction arises from the fact that on passing through the Reynolds number of 2,200 the actual experimental points do not necessarily pass smoothly from the values represented by equation 3 to those represented by equation 5 It is in this respect that the various fluids examined by us show specific differences of behaviour as will now be described

The results on water and acetone are shown in *Figure 5* and were all obtained with the long inlet length of 180 diameters Both liquids continued to obey Poiseuille's law at Reynolds numbers above 2,200 and up to about 3,200 *i e* points were obtained along the prolongation *CD* of the laminar line beyond the critical point Between $R_e = 3{,}200$ and $R_e = 3{,}600$ the pressure drop was higher than corresponded to equation 3 and lower than corresponded to equation 5 However, there were large and rapid fluctuations in the observed pressure and the region $R_e = 3{,}200$ to 3,600 was essentially unstable and marked the point of the actual transition between the two types of flow Above $R_e = 3{,}600$ the points all fell on the line defined by equation 5 and were fairly steady except for very small fluctuations, and these in turn disappeared entirely at a Reynolds number of 3,800 It is to be noted that the above phenomena could be observed whether successive readings were taken with increasing or decreasing rates of flow

The results obtained with the polymer and benzopurpurin solution, using the same inlet length of 180 diameters, are shown in *Figure 6* In both of these liquids there was little or no tendency for laminar flow to persist at Reynolds numbers above 2,200 Thus, unlike water and acetone, there was an almost continuous transition between the lines defined by equations 3 and 5, and the breakdown of the laminar flow was accompanied only by quite small but fairly rapid fluctuations of pressure These disappeared entirely above $R_e = 2{,}800$ It is to be noted that in colloidal solutions there was no evidence of a transition to turbulence at anomalously low Reynolds numbers, such as have been mentioned by OSTWALD[9] and others[9, 10]

The transition in butanol was studied with two different inlet lengths The results marked *Run 2* in *Figure 6* were obtained with the inlet length of 180 diameters and are similar in character to those obtained with water and acetone The liquid remained in laminar flow up to a Reynolds number of about 3,900 Conditions then became very unstable and violent pressure fluctuations occurred On the other hand, if a short inlet length of 42 diameters was in use, the laminar flow broke down quite readily at a Reynolds number of 2,300, only slightly above the critical point The pressure fluctuations were small but fairly rapid It seems, therefore, that the ease of transition is markedly dependent on the amount of disturbance in the flow which persists downstream from the inlet This was confirmed by returning to the use of the long inlet length, but inserting a piece of fine copper wire at its upstream end in order to increase the disturbance The results obtained were almost identical with those for the short inlet length In *Figure 6* these results are marked *Runs 1* and *3*

So far discussion has been confined to the main series of results as obtained with the copper lined steel tube at 20°C As mentioned previously, work was also carried out on the flow of water through a polythene tube and on the possible effect of reduced temperatures The results in the polythene were not significantly different from those obtained in copper-lined steel and there was thus no indication that the wettability of the surface played any appreciable part in the phenomena observed

The work at reduced temperatures was carried out using diethyl ether as the flowing liquid The experiments were performed at the temperatures of melting ice and solid carbon dioxide in acetone The results are shown in *Figure 7* and it is evident that at a given value of the Reynolds number the pressure factor has a fixed value irrespective of the temperature This again confirms the view that the only physical properties of the fluid which are significant are the viscosity and density, their variation with temperature being contained in the Reynolds number

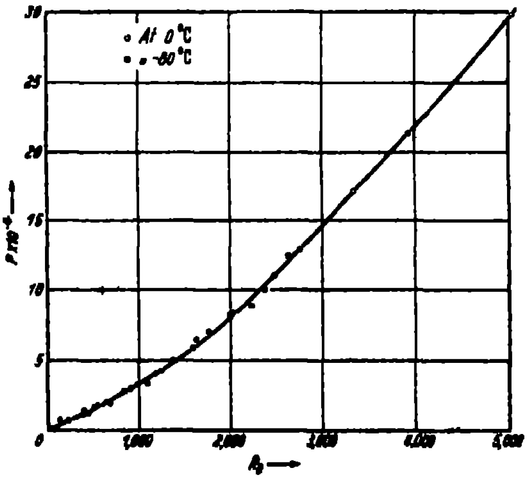


Figure 7 Pressure factor plotted against Reynolds number for diethyl ether at 0°C and − 80°C

It is to be noted that the results of *Figure 7* refer to a coil and are therefore not directly comparable with the earlier results In particular, there is no definite point of transition between two types of flow such as that occurring at $R_e = 2{,}200$ in a straight pipe Rather there seems to be a gradual change from one type to the other over a range of Reynolds numbers from 1,000 to 2,500

CONCLUSION

The experimental results show the remarkable correctness of the Reynolds number in determining the stable type of flow However, there are two important qualifications The first is that the Reynolds criterion can be applied only if there is newtonian flow in the region of low flow rates, otherwise the whole concept of viscosity becomes ambiguous and there is no means of formulating the Reynolds number The second point is that the 'critical' Reynolds number determines the lowest velocity at which turbulent flow can take place (subject to the conditions discussed at the outset), but it does not determine the highest velocity for the occurrence of laminar flow This type of motion can undoubtedly occur at Reynolds numbers greatly in excess of the 'critical' point and to a degree which depends both on the nature of the fluid and on the freedom from disturbance Thus laminar motion in water flowing through a pipe has been observed under favourable conditions at a Reynolds number as high as 50,000[11]

In our own work no very elaborate precautions were taken to avoid disturbance, but the laminar flow has been observed in water and acetone up to a Reynolds number of 3,400, and in butanol which is more viscous, up to about 3,900 In such cases the actual point of transition between the two types of flow is marked by violent fluctuations of pressure, and the measured values of the pressure drop change quite abruptly between the values expressed by equations 3 and 5

The result of using a shorter inlet length was to facilitate the transition between the two types of flow The presence of colloidal particles, as for the polymer and benzopurpurin solutions, seems also to promote the transition

We have regarded the 'critical' Reynolds number of transition as being given by the point of intersection of the lines defined by equations 3 and 5, irrespective of whether or not the transition actually took place at this point, for the latter depends on the degree of disturbance The value of this critical Reynolds number was 2,200 in each of the fluids examined This was in good agreement with results obtained by other observers[5, 11], these usually lie in the range 2,000 to 2,200

It is to be noted that immediately above the transition point the pressure drop continues to be directly proportional to the fluid velocity as is expressed in equation 5 It is only at Reynolds numbers above about 5,000 that the pressure drop varies as the 1 75 power of the velocity as in equation 4 This was also found by NISSAN[12], and the same conclusion may also be drawn from an inspection of the results of STANTON and PANNELL[2]

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Note to Contributors

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Research Correspondence

Obscuration and Smoke Density

IT is customary to estimate the obscuration produced by a natural mist or artificial smoke screen in terms of the visual range The furthest prominent object from the observer that can be distinguished is picked out and its distance measured or located on a map to give what is called the 'visual range' This is related to 'visibility' by what is known as Trabert's law[1] which states that the visual range is proportional to the quotient mean radius of smoke particle mass concentration of smoke The visibility of a given target through a particular type of smoke actually depends on the 'contrast brightness' E, defined as

$$E = \frac{\text{apparent brightness of target} - \text{brightness of background}}{\text{brightness of background}}$$

KOSCHMIEDER[2] has shown that the visual range is given by ln (E/k) k is the optical density which may be written $f\pi n a^2$ where n is the number of particles of radius a, and f is a factor to allow for the variation of transmission of light through a screen of particles with the wavelength λ of the light

In an investigation of the efficacy of smoke screens carried out during the war for the Ministry of Supply we had the opportunity of testing Trabert's law and the results are now published because of their connection with measurements at present being carried out in Britain and North America of the mean drop size found in rain and in fogs, and the resulting effect on visibility in such conditions

The work now reported was carried out inside the pagoda in Kew Gardens (London), which at that time (1942) had large holes made in the floors of the lower storeys, so that it was in effect a vertical chamber of about 100 m^3 capacity A small cordite operated 'gun' was used to disperse a measured volume of liquid (10 – 50 cc) from a height 50 ft above the ground floor level This, mounted in a vertical position in the interior of the pagoda on the fourth storey, is shown in *Figure 1* Smoke density was recorded by three photometers.

Visual range was estimated from time to time by observers who noted the maximum distance at which they could stand away from the windows and yet distinguish the window frames After a period of minutes the smoke cleared by coagulation even in the still air of the chamber

The mean optical density k defined as ln I_0/I, where I_0 is the intensity of light in the absence and I that in the presence of smoke was calculated from the mean of the photo-electric currents.

Typical results are shown in the following tables *Table I* shows how optical density increases with time (at first) and with the quantity of liquid (titanium tetrachloride) *Table II* shows as theory indicates, that the product of optical density and visual range is constant

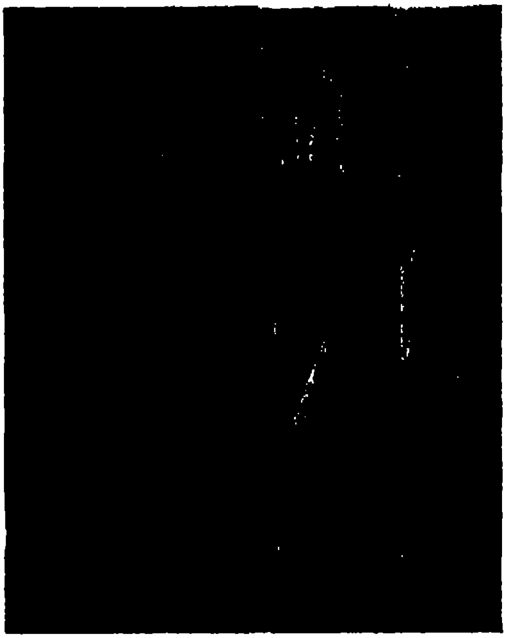

Figure 1 Cordite operated 'gun' used to disperse liquid (Crown Copyright)

At greater concentrations the elementary value of k $(f\Sigma \pi n a^2)$ no longer applies

Table I Variation of Optical Density with Time and with Quantity of Titanium Tetrachloride Dispersed

Volume dispersed cc	*Pressure of ejection lb in^2*	*Mean optical density*	
		½ min	*10 min*
10	250	0·06	0·07
25	250	0·06	0·36
40	290	0·19	0·75
10	350	0·02	0·10
25	450	0·39	0·65
40	480	0·43	0·80

Table II Product of Optical Density and Visual Range

Optical density (k)	0·50	0·21	0·09	0·46	0·59	0·54	0·55	1·0	0·72	1·2
Visual range (m)	1·75	4	6	1·75	1·75	3·5	2·75	1·75	1·5	1·25
k × m	0·8	0·8	0·5	0·8	1·0	1·9	1·5	1·75	1·1	1·5

From the values of optical density and visual range in *Table II* we can derive, using Koschmieder's formula, the value of the contrast brightness, which works out at 0·09 in these smokes.

It is also possible to calculate the mean radius of smoke particle $\bar{a}$, assuming Trabert's law As the volume v dispersed in 1 cc of air is $\frac{4}{3}\pi n\bar{a}^3$, n being now the number of particles in 1 cc, $k = 3v/4f\bar{a}$ or $\bar{a} = 3v/4fk$.

It is also possible to take a sample of the smoke and find its drop size distribution in the ultramicroscope By this means $\bar{a}$ is found to 0 3 μ for these smokes. As the value of f for this size is 2 (*cf* HOUGHTON[3], RICHARDSON[4]), $v = 10^{-7}$ when 10 cc is dispersed in the chamber, and the mean value of $k = 0$ 1 from *Table I* (for 10 cc), so in the formula above we get $\bar{a} = 0$ 4 μ Also $n = 10^6$ from the formula for k which value tallies with the ultramicroscope counts

These experiments are, therefore, in qualitative agreement with Trabert's law

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Voltage Gradients in High Current Spark Channels

THE conducting path existing between two electrodes, after the breakdown processes of electron avalanche formation and streamer propagation[1] have been completed, is known as the spark channel In continuation of earlier research[2] in this laboratory into the characteristics of the spark channel, determinations have been made of the voltage gradients existing in high current sparks in air Currents up to 265 ka have been used and the effect of different electrode materials has been investigated

High current discharges have been studied by NORINDER and KARSTEN[3], but have been limited to currents not greater than 102 ka. Direct oscillographic measurement of the voltage drops across spark channels in air have also been made by HIGHAM and MEEK[4], and FLOWERS[5]. In the latter measurements currents up to 100 ka were studied. An indirect method of determining voltage gradients was used by CRAGGS and MEEK[6] who determined the gradients existing in low current sparks in argon and hydrogen, by calorimetric measurements

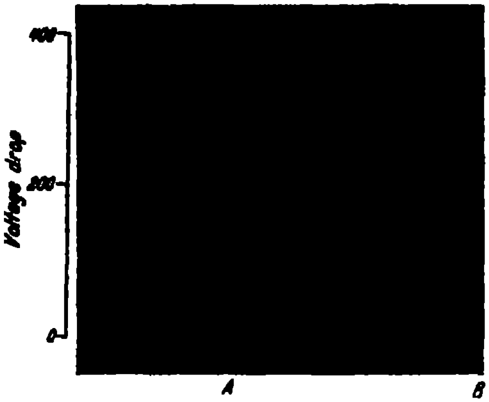

Figure 1 Voltage oscillogram for a 188 ka discharge between copper-tungsten electrodes 3 mm apart Breakdown occurs at A and di/dt = 0 at B The calibration voltage is 400 v and the timing oscillation has a period of 5 microseconds

In order to study high current discharges in this laboratory an impulse generator has been built with which peak currents up to 500 ka have been obtained[7] Using this generator, which has a discharge capacitance of 57μF at 25 kv, the voltage gradients along short spark channels have been determined by oscillographic measurement of the voltage drop across the gap for several gap lengths The voltage and current measurements have been recorded using a 20 kv continuously evacuated cathode ray oscillograph The current waveform was oscillatory and reached its maximum value after 7 7 μsec

The voltage oscillograms were distorted by an induced voltage resulting from the large values of

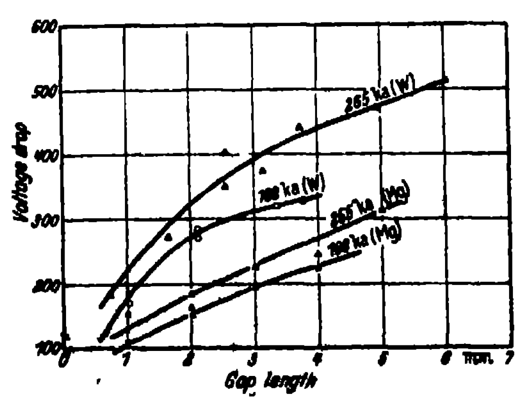

Figure 2. Voltage drops across high current spark channels. W = *tungsten,* Mg = *magnesium electrodes*

di/dt, and for this reason the voltage drop was measured at the instant when this induced EMF was zero i e at the current maximum when di/dt = 0 To obtain oscillograms suitable for accurate measurement (i e of small slope dv/dt when t = 7 7 μsec) the above induced voltage in the measuring circuit was reduced by subtracting the voltage which appeared across a suitable mutual inductance coil If the induced voltage recorded is expressed in the form M di/dt then the quantity M varies during the first few microseconds of the discharge[8] because the diameter of the conducting path varies greatly during this period As a result it was not possible to cancel completely the induced voltage and obtain an oscillogram showing the variation of the discharge voltage as a function of time

One half of the spark gap voltage was applied to the deflection plates of the oscillograph by means of a potential divider and matched concentric cable. This oscillograph could withstand one half of the pre-breakdown voltage without damage, and the deflections after breakdown were adequate for measurement as can be seen in the typical oscillogram given in *Figure 1*

Some results are given in *Figure 2* for tungsten and magnesium electrodes Tests were also performed with copper-tungsten electrodes, but the effect of the copper was not detectable The measurements show that the gradients are high and increase with increasing current in the range studied (188–265 ka) From the graphs it is evident that, with the volatile magnesium electrodes, the metal vapour had an appreciable effect on the discharge It is not known at present whether tungsten vapour appreciably affects the discharge in the time involved, but relevant investigations will be undertaken

These experiments emphasize the fact that long gaps are desirable, if sparks in pure gases are to be studied[2–4], as short gaps soon become contaminated by metal vapour from the electrodes[7, 8] Velocities of migration of metallic vapour clouds up to 2 1 × 10^6 cm/sec (for Zn) during the first 0 27 μsec of the discharge have been measured by LAWRENCE and DUNNINGTON[9], and similar results have been reported by later workers[8] Experiments are in hand to produce a long high current spark from the high current generator, in conjunction with a high voltage generator, using a circuit described by SOLOMONOV[10], and developed independently in this laboratory by DURNFORD and MCCORMICK[11]

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Adsorption of Cobalt Naphthenate by Cellulose Fibres

COBALT soaps, such as the naphthenate and linoleate, are added to linseed oil varnishes used in printing inks to catalyse the autoxidation reaction, which results in the varnish changing from a liquid state to a solid one In practice it has been found that this gelation is retarded by some types of paper, particularly those papers which, when they are extracted with hot water, yield extracts of low pH It was considered possible that the inhibition might be due to adsorption of the cobalt soap by the cellulose fibres Preliminary experiments have demonstrated that adsorption of cobalt from solutions of cobalt naphthenate in oil (linseed and olive) on paper can occur, and it is felt that a note indicating the existence of the phenomenon may be useful at this stage Later, it is hoped to study the adsorption in greater detail and to ascertain its importance to the general problem of drying of inks on paper

EXPERIMENTAL

The work to date has been done on a *Whatman No 1* filter paper as supplied and on the same paper acidified with hydrochloric acid and sulphuric acid In all cases the experiments were made with the paper conditioned at a fixed relative humidity

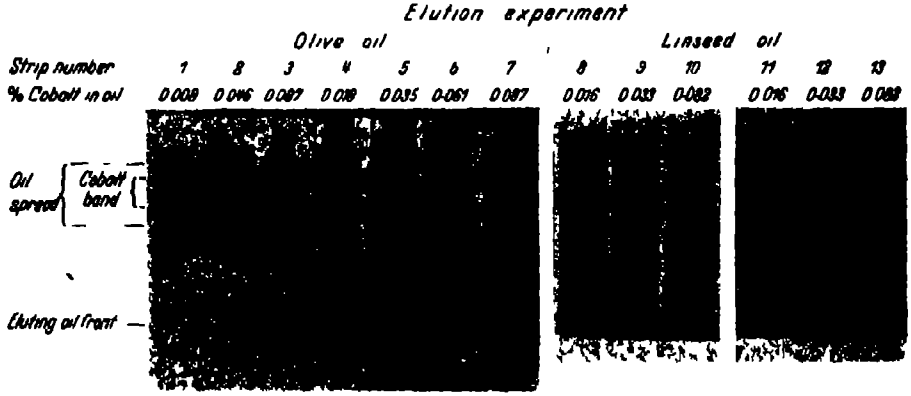
Three types of experiment were made

1 'Spreading' experiments—A narrow band of cobalt naphthenate solution in oil was run across a strip of paper, and after spreading for an arbitrarily chosen time the cobalt band was developed with rubeanic acid[1] The cobalt band on acid paper was much narrower than the width to which the oil had spread. On non-acid paper the cobalt band width was dependent upon the concentration of the applied solution and at the highest concentration was as wide as the oil band

2 Elution experiments—The above experiments were repeated in all detail except that prior to development the applied band was eluted with oil using normal chromatographic techniques Upon development the cobalt band was found to be of the same width and in the same position as in the non-eluted case Typical results with olive oil solutions are shown on *Figure 1*, strip *1-7* *Figure 2* shows the measured cobalt band width as a function of concentration for two experiments with olive oil solutions, which differ only in the extent to which elution was allowed to proceed The line representing the non-acid papers shows clearly that the band width is dependent only on concentration and not on elution The results for the acid paper show a much smaller dependence on concentration within the range studied, suggesting that the adsorptive capacity of the paper is greater than the amount of cobalt which has been applied, even at the highest concentration used In a further experiment elution with petroleum ether following oil elution produced a band in the same position and of the same width as the one observed after a single elution with oil This irreversible adsorption observed with olive oil as solvent was also found with linseed oil on acid paper, strips *8* to *10*

Experiments using linseed oil as solvent for the cobalt naphthenate are complicated by the ability of the linseed oil to oxidize to a gel Because of this some interesting results have been obtained With the non-acid paper at low cobalt concentration, strip *11*, the cobalt has moved down the strip with the eluting oil but at higher concentrations the oil has been stopped at the band of application of the cobalt, strips *12* and *13* This latter effect is presumably due to the band of cobalt naphthenate solution in oil having gelled between the time of application and the time of elution A comparison of this result with that on the acid paper (strips *8* to *10*) suggests that the adsorbed cobalt on the acid paper is less active in promoting gelation

3 Capillary rise experiments—*Figure 1* (strips *14* to *21*) shows the result of an experiment in which a solution of cobalt naphthenate in olive oil was allowed to



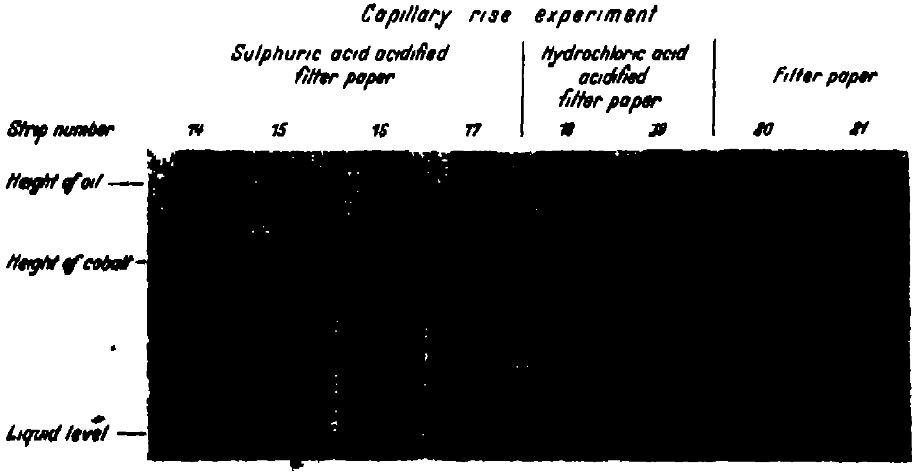

Capillary rise experiment
Sulphuric acid acidified filter paper
Hydrochloric acid acidified filter paper
Filter paper
Strip number
14
15
16
17
18
19
20
21
Height of oil
Height of cobalt
Liquid level

Figure 1

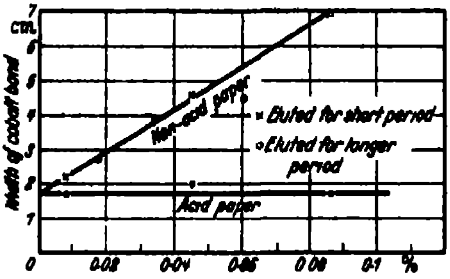


Figure 2 Cobalt band width as function of cobalt concentration in oil

rise up strips of paper and acidified paper The ratio of the height of rise of cobalt to the height of rise of oil affords a measure of the relative adsorptions The results are summarized in *Table I*

Table I Height of Rise of Cobalt up Strips of Paper

Paper and relative humidity of experiment	*Ratio of cobalt height to oil height*	*Gm acidic hydrogen per gm paper*
Filter paper 65 per cent R H	0 88	0
HCl *acidified filter paper 65 per cent R H*	0 07	—
H_2SO_4 *acidified filter paper 65 per cent R H*	0 72	0 000127
H_2SO_4 *acidified filter paper 100 per cent R H*	0 67	0 000175

Figure 1 and *Table I* show clearly the influence of acidity on the adsorption These experiments have shown that cobalt can be irreversibly adsorbed from olive oil or linseed oil solutions on acidified filter paper and from olive oil solutions on non-acid paper It is also apparent that with linseed oil the adsorption inhibits the drying

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The Dielectric Properties of Copper Oxide Rectifiers

Audiofrequency measurements of the barrier layer capacitance are often made on metal rectifiers, because they yield from the Schottky capacitance relationship[1] a value for both the height of the potential barrier at the contact and the density of the ionized impurity centres in the barrier layer. The capacitance is generally assumed to be independent of frequency, but recently published measurements[2] on selenium rectifiers have shown this assumption to be incorrect

Measurements of the barrier layer capacitance *C* and differential resistance *R* have now been made at frequencies between about 100 c/s and 10 kc/s on a number of copper oxide rectifiers An impedance bridge was used, the circuit of which enabled AC to be superposed as a small ripple, about 30 mv in amplitude, on the constant DC bias Errors due to stray impedances were eliminated by a Wagner earth device and the measuring arm of the bridge was compensated for the effect of the small resistance due to the layer of semiconductor in series with the barrier layer

It was found that with increase in frequency the capacitance *C* decreased in the manner illustrated in *Figure 1* The differential resistance *R* also varied with frequency, and was smaller than the corresponding value obtained from the slope of the DC current/voltage characteristic The effect can be described by supposing that in the conventional rectifier equivalent circuit a frequency dependent resistance R_f is connected in shunt with the DC differential resistance R_d to give a combined resistance *R*

The above procedure enabled the loss angle tangent, $\tan\varphi = 1/RC\omega$, of the barrier layer to be split into two components, one due to the DC resistance R_d and the other due to the frequency dependent resistance R_f The latter component was obtained from the equation

$$\tan\varphi' = (1/RC\omega) - (1/R_fC\omega)$$

where $\omega = 2\pi f$ is the angular frequency

In *Figure 1* values obtained at 18°C for the capacitance of a rectifier with approximately 0 4 v DC bias applied in the blocking direction are plotted together with corresponding values of $\tan\varphi'$ The curve drawn through the experimental loss angle points is a theoretical Debye absorption curve, calculated for a maximum loss angle tangent of 0 0295 occurring at 600 c/s Great accuracy cannot be claimed for the values of loss angle plotted on *Figure 1* because the differences observed between R_d and *R* were small. The errors were greatest at low frequencies and their possible magnitude is shown on the curves for 18° in *Figure 1*

Measurements were also made on the same rectifier at + 40°C and 0°C. The maximum loss angle tangent was found to be different at both of these temperatures from that obtained at 18°C, but it cannot be stated whether or not this effect was due to a temperature change alone, because the bias voltage was varied to obtain the best conditions for

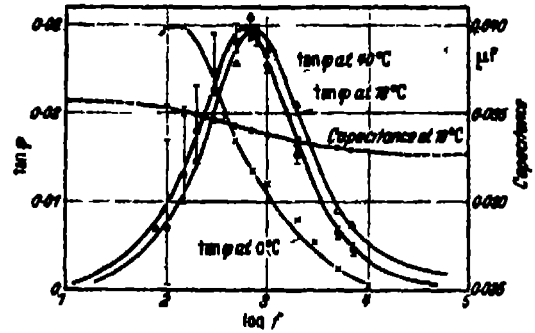

Figure 1 *Dispersion and absorption in* Cu_2O *barrier*

measurement of tan φ′ In *Figure 1* normalized values of tan φ′ obtained at 0° and 40°C are also plotted and show that the absorption curve had shifted to lower frequencies as the temperature decreased The measurements do not cover a large enough range of temperature to enable a reliable estimate of activation energy to be made At temperatures higher than 40°C the DC resistance of the barrier layer was low enough to swamp the absorption effect Below 0°C the absorption peak occurred at low frequencies, and the bridge was insensitive to capacitance change Another method of measurement will be required to extend the observations to lower temperatures

The mechanism of the effect has not yet been established Since cuprous oxide is a reserve semiconductor the relaxation mechanism described by Goodman, Lawson and Schiff[3] cannot be excluded, but the fact that the loss angle tangent curves were within broad experimental limits, symmetrical with respect to log (frequency) suggests this mechanism is not responsible for the observed effects An alternative mechanism is that dispersion and absorption arise from the motion of Cu^+ ions in the barrier layer, as cuprous oxide is known[4] to possess a small ionic conductivity due to the migration of Cu^+ ions A value of 6×10^{17} lattice defects per cc at 18°C was obtained from a calculation similar to that made by Breckenridge[5] for absorption due to lattice defects in alkali halide crystals In our calculation it was assumed that the ions migrated by Schottky defects (due to missing Cu^+ ions), that the distance between neighbouring Cu^+ ions was 3 Å, and that the dielectric constant of cuprous oxide at high frequencies was 12 The density value obtained is not unreasonable.

Although the mechanism causing the observed effects is still uncertain, the measurements have established that at audiofrequencies both the capacitance and differential resistance of copper oxide barrier layers depend upon the frequency of measurement. It is hoped to elucidate the mechanism by further experiments which are in hand

The authors wish to acknowledge the assistance given by the Westinghouse Brake and Signal Co Ltd, who kindly supplied the rectifiers used for the experiments

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A Simple Method for Measuring the Movement of Insoluble Monolayers at Air/Water Interface

The technique for the measurement of force/area curves of insoluble monolayers has recently been described by Alexander[1], if elasticity, compressibility and re-expansion of monolayers are to be studied, it is advantageous to supplement the study with a method which allows measurement of the exact movement of the monolayer To this end we used a rectangular glass trough with dimensions 13 × 49 × 0·4 cm, the glass of the bottom of the trough had the same thickness as a microscopical slide The trough was placed on the table of a microscope in such a position as to allow the observation of the monolayer up to an enlargement of 500 times Polarized light was conveniently obtained by means of *Polaroid* The film was spread on a clean surface with an *Agla* pipette and compressed in the usual manner to give the force/area curve (*Figure 1*) The convex and linear parts show the different pressure regions characteristic for a given protein After cleaning the surface the mica-float was replaced by a fixed glass slide and the film was spread once more The movable glass slide was slowly moved into a position where only a pressure of 0·5 to 1·5 dyne/cm was exercised (*Figure 1*, circle) Then a glass rod (or glass wool) of about 4 cm length was gently placed on the monolayer so as to be visible in the right hand region of the ocular-micrometer; slight pressure now applied moved the glass rod from right to left, thereby showing the compression of the monolayer, on re-expansion it moved from left to right again. The glass rod eliminated vaselined threads, upon slightest pressure the glass rod showed

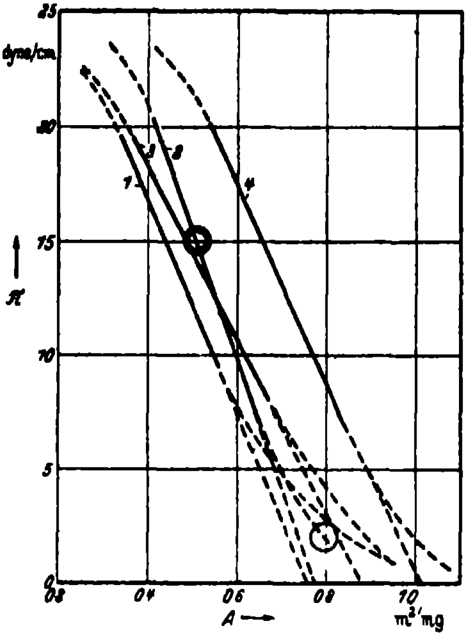

Figure 1 Force/area curves of thrombin on buffered saline of pH 2 (curve 1), pH 7 (curve 2), pH 11 (curve 3) and of serum albumin pH 7 (curve 4) The circle indicates microscopically observed regions

a free and steady movement, thereby proving that it had not pierced the monolayer As long as the latter consists of gas and islands, to quote HARKINS and BOYD[2], the movements of the glass rod have a tendency to be erratic, but as soon as the limiting area is decreased, so that the monolayer is liquid-expanded, it appears perfectly steady In the low pressure region of about 1 dyne/cm a magnification of 13 5 times is appropriate (*Figure 2a*), whereas in the intermediate region of 10 to 19 dyne/cm (*Figure 1*, double circle) a magnification of 100 times is preferable (*Figure 2b*) As our drive mechanism advanced the movable glass slide 1/4 mm per round the resulting reduction of the limiting surface was 0 325 cm² or 1 65 per thousand Such an advance of the glass slide gave a compression of the monolayer of 30 μ (*Figure 2b*) and the resulting surface pressure was 0 075 dyne Repeated experiments have shown that pressures of 0 012 dyne ± 0 002 dyne could be read

Fresh preparations of *Thrombin* (Hoffmann-La-Roche, Basle) and of *Serum Albumin*, human (Swiss Red Cross, Plasma fractionation service) were spread together with 0 2 per cent isoamylic alcohol on buffered saline Pressure was exercised within 10 min of spreading at room temperature of 18° The values for A_0 may be compared with those of DERVICHIAN[3], who found A_0 for *Euglobulins* 0 53 and for *Pseudoglobulins* 0 34 at *p*H 4 5 The coefficient of compressibility M_s was calculated from formula given by NEURATH and BULL[4]

Figure 2a

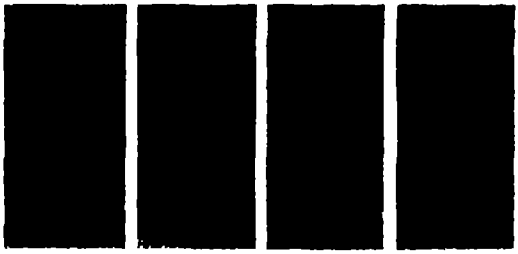

Figure 2b

Figure 2 a glass rod movement liquid expanded region, 13 5 × b intermediate region, 100 × Reduction factor ½ on reproduction for a and b

Table I

	Thrombin			*Albumin*
*p*H	2	7	11	7
Buffer 0 01 mol	0 01 N HCl	Na_2HPO_4 KH_2PO_4	Na_2HPO_4 KOH	Na_2HPO_4 KH_2PO_4
$A_0 \frac{m^2}{mg}$	0 76	0 78	0 88	1 09
$M_s \frac{dyne}{cm}$	− 0 60	− 0 48	− 0 57	− 0 42

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Chairman's Note

At the end of this the third volume of *Research* it is appropriate to review the aims of the journal and to ask whether it is in fact fulfilling its functions

In my Editorial in the opening issue of *Research* I made the point that ' all practical applications have their origin in pure research There is always a wide gap between initial research and practical development based upon it The time lag can be reduced—in many cases greatly—by the creation of a greater awareness of possibilities on the part of all concerned, the scientist, the technologist, the industrialist and even the general public '

These then are the aims—to assist regular readers to keep abreast of progress in all fields of scientific endeavour , to make men of science more readily aware of the possible practical bearing of their work , to stimulate and guide industrialists by pointing out where science can contribute to the greater efficiency of their work

The criticism has sometimes been levelled against *Research* that some of the review articles are too limited in scope and appeal , in other words, that they are too specialized This raises two separate and distinct points, the subject to be reviewed in the article and the method of reviewing it It is doubtful whether the subject matter of an article can ever be said with any degree of certainty to be too specialized There are many examples of results obtained in research which appear to have very limited application proving to hold the key to advances in quite different and seemingly unrelated fields Such cross fertilization of ideas is in fact one of the chief aims of *Research*

The second point raised may have more substance In the past some authors may not have been made fully aware of the wide readership of the journal and a minority of articles may therefore have been written in such a way as to be intelligible only to a limited number of scientists A new list of suggestions for authors is being drawn up It will be made quite clear that while *Research* is not a journal of popular science its readership is very wide and covers every branch of science and industry Authors will be asked to bear in mind that their article should be intelligible to all who have a certain basic scientific knowledge , possible practical applications should also be stressed

Research continues to provide a rapid publication service for short communications in its ' Research Correspondence ' Letters are published in from two to six weeks of receipt, which is the shortest time possible for a monthly journal In order that this standard may be maintained authors are specially requested to note that letters should have a maximum length equivalent to 750 words inclusive of illustrative material

In conclusion, *Research* will continue to bring the potential practical applications of scientific research before as wide a readership as possible, whether of scientists working in pure or applied science, or of industrialists who will use the results of science to improve the efficiency of their undertakings

Superconductivity

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THE phenomenon of superconductivity constitutes one of the two major problems confronting the theoretical physicist today Just as the nature of nuclear forces has eluded an explanation based on first principles, so has superconductivity defied all attempts to develop a molecular theory elucidating all of its aspects On the other hand, the phenomenology of the subject, including the electrodynamic and thermodynamic descriptions, seems adequate Thus the experimental investigator is faced with the problem of providing new information which may yield the key to the fundamental understanding of the phenomenon It is the purpose of this paper to review the present state of knowledge in this field and to indicate the paths which current research are taking

In 1908 H KAMERLINGH ONNES discovered the first evidence of the complete absence in mercury of electrical resistance at a characteristic low temperature The temperature at which the transition between normal and superconductivity occurs is a function of the magnetic field in which the substance finds itself, the critical field being zero at the highest temperature at which the superconductive state may exist and increasing to a finite value less than 3,000 oersted at the absolute zero Some seventeen metals have been found to exhibit the phenomenon , of these niobium has the highest transition temperature, 9 22° K It should be noted that some of the best ordinary conductors *e g* copper, silver, and gold, do not become superconductive at temperatures as low as 0 05° K In addition to pure metals a large number of alloys of two or more metals in solid solution, of intermetallic compounds, and of semi-metallic combinations of metals with hydrogen, carbon, nitrogen, silicon, boron, and sulphur become superconductive

The ability of a magnetic field to destroy superconductivity was discovered by Kamerlingh Onnes in 1914, but it took almost twenty years before the fundamental magnetic properties of superconductors were established. Even today it appears that most scientists, not working in the field of low temperature physics, are not aware of the fact that the magnetic properties of a superconductor are fully as fundamental and as unusual as are the electrical properties

To determine the magnetic properties of a superconductor in the light of the facts already presented the case of a singly connected superconductor is first considered Predictions will be based on Maxwell's equation relating the time rate of change of the magnetic induction **B** and the electric field **E** within a body

$$\dot{\mathbf{B}} = -c\,\mathrm{curl}\,\mathbf{E} \qquad (1)$$

Since **E** = 0, $\dot{\mathbf{B}}$ = 0, and **B** remains constant, as long as the body is superconductive, and equal to the value of the magnetic induction within the body when it passes into the superconductive state. Suppose, for example, that the body is cooled in the presence of a magnetic field **H** to a temperature below which it becomes superconductive in a field of this magnitude We predict that there will be ' frozen in ' magnetic induction **B** = **H** which will be maintained even if the original field is reduced to zero On the other hand, if the body is cooled in the absence of field to some temperature below the transition temperature, then the magnetic induction **B** will remain zero if a small external field is applied But if the magnetic field is increased to a value above the critical one, superconductivity will be destroyed, and we will have approximately, **B** = **H** Now if the field is reduced, the body will pass into the superconductive state with the value of the magnetic induction within it equal to $\mathbf{H}_c$, the critical field corresponding to the given temperature, and this will remain constant so long as **H** is not made greater than the critical field *Figure 1* shows this predicted behaviour for a sphere Additional complication is introduced by the non-zero demagnetization coefficient of the specimen Thus penetration begins at **H** = ⅔ $\mathbf{H}_c$ simply because, at this value of the applied field, the sphere finds itself in a field equal to $\mathbf{H}_c$ In particular, the outstanding hysteresis in the transition is to be noted

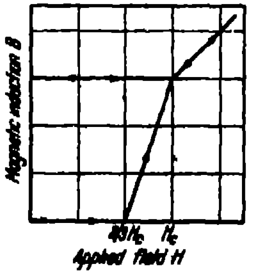

Figure 1 Magnetic properties of a perfectly conductive sphere as deduced from Maxwell's equation

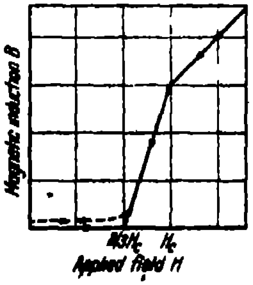

Figure 2 Magnetic properties of a superconductive sphere at constant temperature

In 1933 it was discovered by W MEISSNER and R OCHSENFELD[1] that these predictions are radically at variance with the experimental facts They found

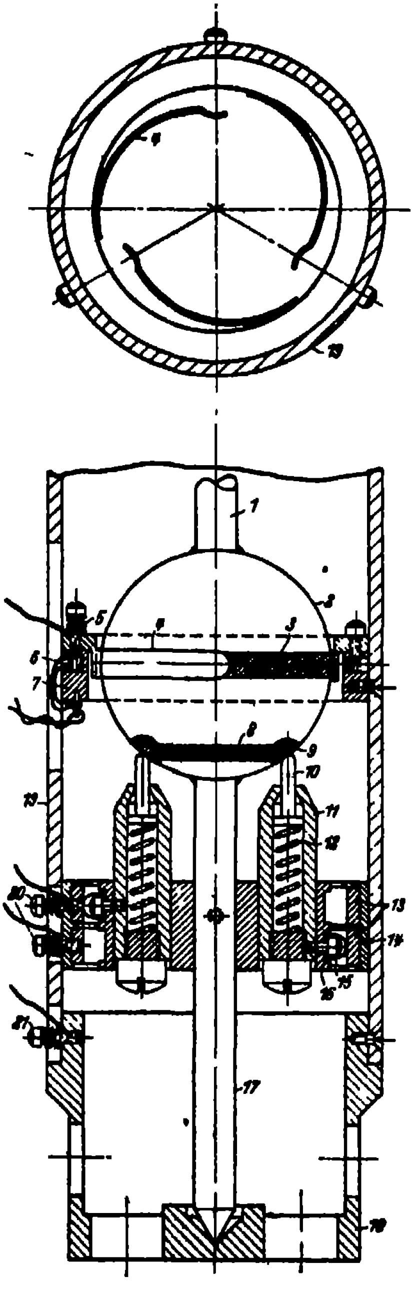

Figure 3 Details of rotor assembly

1 Copper rod connecting sphere to drive shaft
2 Lead sphere
3 1/2 mil thick gold plated band
4 Phosphor bronze lead spring contact
5 Spring loaded contact screw
6 Pick-up coil for B,H measurement 108 turns of No 42 enamelled copper wire, average diameter 1 080 in (2 74 cm)
7 *Plexiglas* holder
8 Graphite film thermometer
9 Evaporated gold contacts
10 Copper contact
11 Spring retainer
12 Phosphor bronze loading spring
13 Stationary brass contact rings
14 *Plexiglas* stationary contact holder
15 Phosphor bronze leaf spring contact
16 *Plexiglas* moving contact holder
17 Copper rod electrode
18 Brass bearing and contact block
19 Main *Plexiglas* support tube
20 Spring loaded contact screws
21 Spring loaded contact screws

that just as the electrical resistivity of a superconductor is zero and independent of its previous history, so also is the magnetic induction equal to zero irrespective of the value of the induction existing within the body when it becomes superconductive For a sphere, the isothermal changes, below the transition temperature, of the magnetic induction are given as a function of field in *Figure 2* These results are to be contrasted with those predicted from Maxwell's equations and the zero resistivity of a superconductor, as shown in *Figure 1* The small hysteresis, indicated by the dashed return curve, is always observed to some extent in practice It is believed, however, to be of subsidiary importance and to be due to non-homogeneity This point may be clarified by a discussion of the magnetic properties of multiply connected superconductors Considering a specimen of a superconductor which has a hole within it, while the Meissner effect means that **B** within the body itself will be zero so long as it is superconductive, it carries no implication with respect to the hole Equation 1 may however be integrated over a surface through the hole and bounded by the superconductor The result is

$$\int_s \mathbf{B}\, d\mathbf{S} = -c\int_s \text{curl}\,\mathbf{E}\, d\mathbf{S} = -c\oint \mathbf{E}\cdot d\mathbf{l} = 0 \qquad (2)$$

Thus the total flux threading the hole must remain constant and equal to that obtaining when the surrounding body became superconductive This deduction has been abundantly confirmed by experiment[8] Inhomogeneous regions in a singly connected superconductor may behave as normally conductive holes, so that the presence of small hysteresis in magnetic transitions is probably not of basic import.

Because of the fundamental nature of the magnetic properties of superconductors it may be worth while to indicate how these may be demonstrated At the same time it will be convenient to illustrate some of the techniques used in low temperature investigations. Usually the magnetic properties of superconductors are studied with the aid of stationary or flip coils

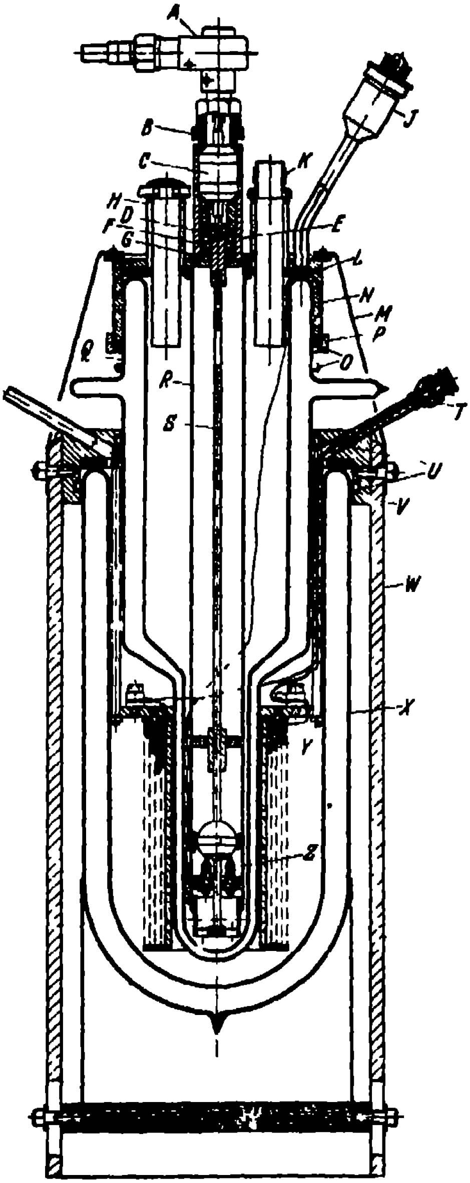

Figure 4 Liquid helium cryostat

A Right-angle gear
B Gear box retaining nut
C Interchangeable gear box
D Packing retainer
E Ball bearing
F Garlock seal
G 'O' ring
H Manometer and gas vent line
J Wire seal
K Filling and pumping line
L Felt gasket pad
M Brass support brace
N Brass dewar cap
O 'O' ring
P Cap nut
Q Helium dewar
R Main *Plexiglas* support tube
S Thin wall monel drive shaft
T Gas tight solenoid power plug
U Rubber tube dewar seals
V *Micarta* nitrogen dewar cap
W Brass uprights
X Nitrogen dewar
Y Liquid nitrogen cooled solenoid
Z Rotor assembly (see *Figure 6*)

or with bismuth wire probes. An ingenious and direct method was recently introduced by W. V. HOUSTON and C. F. SQUIRE[4,5]. These workers studied, as a function of temperature, the voltage induced in a lead sphere rotating as a Faraday disk in a constant axial magnetic field. With sliding contacts at the axis and the periphery of the sphere, the unit becomes a homo-polar generator the output voltage of which is

$$\varepsilon = \Phi\omega/2\pi \qquad (3)$$

where Φ is the total magnetic flux threading the great circle of the sphere normal to the axis and ω is its angular velocity. Thus the induced voltage is proportional to the magnetic induction within the sphere. A. WEXLER and W. S. CORAK[5,6] studied in detail the isothermal ε,H curves for a one inch (2.54 cm) lead sphere rotating in liquid helium. A number of rotational speeds up to 10,800 rpm were involved. It was expected that these curves would be exactly of the form of *Figure 2*. After the sphere had been exposed to a magnetic field $H > \frac{2}{3}H_c$, then even in the absence of an applied field there is a measurable output, for the presence of 'frozen flux' makes the rotor a unipolar generator producing an output voltage given by equation 3. *Figure 3* shows the rotor assembly; in *Figure 4* it is shown mounted in place in the liquid helium cryostat. *Figure 5* presents typical data obtainable by this method. The results are of the form shown in *Figure 2*. Those points on the curves of *Figures 2* and *5* corresponding to $\frac{2}{3}H_c < H < H_c$ belong to a state in which the electrical and magnetic properties of the conductor are intermediate between those of the normal and those of the superconductive phases. This is known as the intermediate state. A considerable amount of theoretical[7-9] and experimental[10-13] work on the microscopic structure of that state has been done; the agreement between theory and experiment is generally quite good.

It has been pointed out[14] that critical data should be obtained by magnetic rather than electrical measurements, for the magnetic properties of a material represent a volume effect while the electrical resistance may be determined by paths of least resistance, which actually occupy but a small part

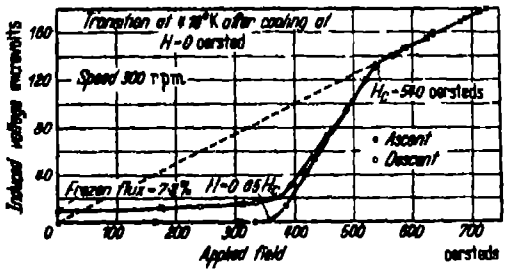

Figure 5 Transition at 300 r p m

of the bulk of the sample Moreover, from the magnetic data, the fraction of superconductive material may be estimated

The first step in the understanding of the mechanism of a phenomenon is the formulation of the thermodynamic considerations governing it This has been done for the superconductive transition by A J Rutgers[15] and by C J Gorter and H B G Casimir[16], and the consequences have been most fruitful Taking the Meissner effect as evidence that conditions of thermodynamic reversibility apply to the superconductive transition, these investigators considered the $\mathbf{H},T$ curves as representing the locus of points at which the superconductive metal and the normally conductive metal, considered as separate thermodynamic phases, are in equilibrium The equating of the free energy functions leads to a relation analogous to the Clausius-Clapeyron relation for a liquid/vapour system

$$S_N - S_S = -\frac{V\mathbf{H}_c}{4\pi}\frac{d\mathbf{H}_c}{dT} = \frac{L}{T} \qquad (4)$$

where S is the entropy, V the volume of the unit considered, and L is the latent heat of the transition Differentiation of equation 4 with respect to temperature gives the heat capacity difference between the two phases

$$C_N - C_S = T\frac{d}{dT}(S_N - S_S)$$

$$= -\frac{VT}{4\pi}\left[\left(\frac{d\mathbf{H}_c}{dT}\right)^2 + \mathbf{H}_c\frac{d^2\mathbf{H}_c}{dT^2}\right] \qquad (5)$$

Equation 4 predicts zero latent heat of transition both at the transition temperature and at the absolute zero The validity of these predictions, as well as the point by point agreement between the thermal quantities deduced from magnetic data by J. G Daunt and K Mendelssohn[17] and the directly measured quantities for tin as determined by W H Keesom and P. H van Laer[18], are shown in *Figure 6.*

J A. Kok[19] and Daunt and Mendelssohn have carried the thermodynamic considerations a step further and have shown how to compute from the $\mathbf{H}_c,T$ curve the electronic entropy and the heat capacity of the normal metal This is of special value because the method circumvents the difficulties attending the direct measurement of these quantities, which arise, of course, from the relatively large contribution by the lattice to the entropy At very low temperatures the heat capacity of a normal metal is accurately represented by a linear term in T plus the Debye T^3 lattice term

$$C_v = \gamma T + 464\cdot 4\left(\frac{T}{\Theta}\right)^3 \qquad (6)$$

From equation 6 it follows that the entropy is

$$S = \int_0^T \frac{C_v}{T}\,dT = \gamma T + 154\cdot 8\left(\frac{T}{\Theta}\right)^3 \qquad (7)$$

Since it has been found experimentally that the heat capacity of a superconductor near the absolute zero follows approximately a T^3 law and in particular does not contain a linear term in T, it follows that the slope at absolute zero of the $S_N - S_S, T$ curve for a metal as calculated from equation 4 gives the electronic entropy of the normal metal Further, the difference between the tangent at absolute zero and the curve gives the electronic entropy of the superconductive metal The electronic entropy for the normal metal, as calculated in this way, is appreciably higher than that calculated by

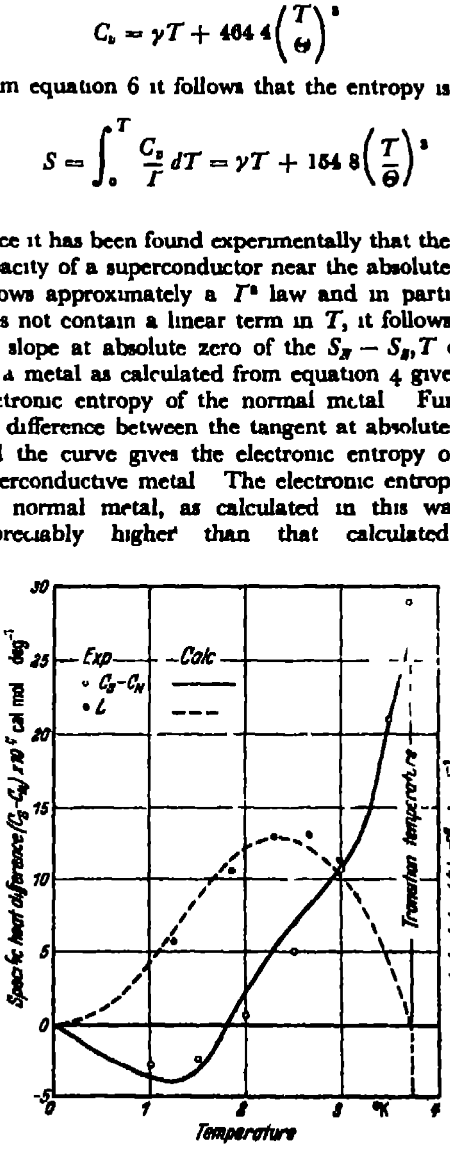

Figure 6 Comparison of calculated and observed differences in the thermal properties of tin in the normal and superconductive states

A. SOMMERFELD's formula[20] on the assumption that the number of free electrons is equal to the valency. The conclusion drawn by Daunt and Mendelssohn in the case of tantalum and niobium is that not only the valence electrons but also the electrons in the partly filled lower shell take part in the formation of the superconductive state Recently, these considerations have been applied by J G DAUNT and C V HEER[21] to the threshold curves of superconductive aluminium and zinc There is still some question regarding the applicability of the thermodynamic treatment to such hard superconductors as those in the vanadium, niobium, tantalum group, the difficulty here appears to be in securing specimens exhibiting reversible behaviour, and the key to this situation probably lies in the metallurgy of these metals

The thermodynamic description of superconductivity, which has led to a correlation of a number of its aspects and the prediction of new properties, must be considered along with the electrodynamic description of F LONDON and H LONDON[22,23] for a complete understanding of the macroscopic features of the phenomenon Together, these act as a guide for all mechanistic discussions It has been seen previously that Maxwell's equations do not predict the magnetic properties of superconductors if the zero resistivity is the only property which is considered The essential feature of the Londons' theory based on the experimental evidence of superconductivity is the assumption of the validity of the following relation between the magnetic field acting on a superconductor and the current it carries ·

$$-\mathbf{H} = \Lambda c \operatorname{curl} \mathbf{i} \tag{8}$$

If this equation is combined with Maxwell's equation $c \operatorname{curl} \mathbf{H} = 4\pi \mathbf{i}$, it follows that

$$\frac{\partial^2 \mathbf{i}}{\partial x^2} + \frac{\partial^2 \mathbf{i}}{\partial y^2} + \frac{\partial^2 \mathbf{i}}{\partial z^2} = \frac{4\pi \mathbf{i}}{\Lambda c^2} \tag{9}$$

and

$$\frac{\partial^2 \mathbf{H}}{\partial x^2} + \frac{\partial^2 \mathbf{H}}{\partial y^2} + \frac{\partial^2 \mathbf{H}}{\partial z^2} = \frac{4\pi \mathbf{H}}{\Lambda c^2} \tag{10}$$

From equation 10 it may be deduced that for $\mathbf{H} < \mathbf{H}_c$, the magnetic field falls off exponentially as a function of the distance from the surface, such that it attains $1/e$ of its value at the surface in a distance $\lambda = c\sqrt{\Lambda/4\pi}$ Now $\Lambda = m/ne^2$, where m is the effective electron mass, e its charge, and n the number of superconductive electrons per unit volume The experimental determination of the manner in which a magnetic field penetrates a superconductor is thus of fundamental importance If experiment shows the predicted penetration of the field, the data may be used with some confidence to deduce the quantity n/m and its variation with temperature

The depth of penetration λ may be studied by several methods which fall into two categories : one dealing with superconductors of dimensions comparable with the penetration depth and the other dealing with macroscopic samples By solving equation 10 for particular geometric cases with boundary conditions determined by the external magnetic field, one can obtain relations involving the critical fields for the specimens used, the threshold field for the bulk material, and two parameters having the dimensions of length one related to the dimensions of the specimens and the other the penetration depth. E T S APPLEYARD and his collaborators[24, 25] have applied these considerations to mercury films Their results were in approximate agreement with the theoretical predictions and hence their numerical value of $\lambda = 1\ 2 \times 10^{-5}$ cm at 2 5°K is to be considered approximate However, the values of the penetration depths as a function of temperature relative to that at a given temperature are more reliable The results are shown in *Figure 7* along with those of D SHOENBERG[26] for mercury globules in colloidal suspension H B G CASIMIR[27] introduced the method of obtaining the relation between λ and temperature from the variation of the apparent susceptibility of a macroscopic superconductor as determined by a mutual inductance method Using this procedure, E LAURMANN and D SHOENBERG[28] obtained data of the form already presented, but with the added feature, that for tin λ depends somewhat on the relative direction of the magnetic field and the crystallographic axes Still another method was used by H LONDON[29] who measured the eddy-current heating of a superconductor in a high frequency alternating field If, in addition to superconductive electrons, there exist electrons capable of carrying an ordinary current, then, at frequencies at which the inertia of electrons must be considered, eddy currents with attendant Joule heating should appear The initial experiments, performed at a wavelength of 20 5 cm, gave results in qualitative agreement with *Figure 7* A B. PIPPARD[30] and the Massachusett Institute of Technology group[31] have recently extended the work to higher frequencies The high frequency studies have several interesting fundamental aspects, and the work is being continued actively in this field. Among these is the possibility of computing the number of free electrons per atom, in addition, certain anomalous effects appear in the low temperature impedance of normal metals at high frequencies The work on the penetration of a magnetic field into a superconductor has resulted in a clear picture of its temperature dependence and of its approximate value Its potentialities, however, have not as yet been fully realized.

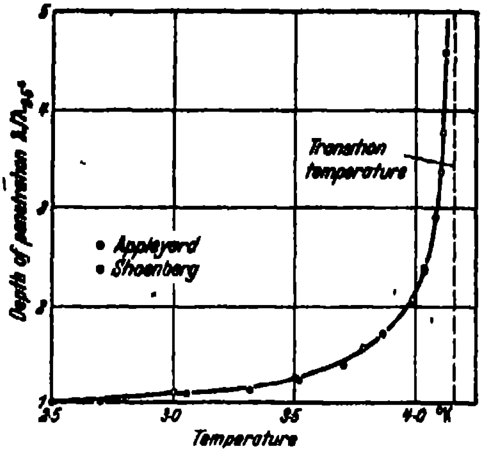

Figure 7 Temperature dependence of the depth of penetration of a magnetic field into superconductive mercury

The phenomenological theory of the Londons serves to establish a check on mechanistic theories While a number of attempts at mechanistic theories have been put forward[34-36], *none is free of criticism*[37] on the basis of the Londons' theory

The foregoing covers the fundamental features of superconductivity There exists, in addition, a rich bibliography pertaining to the study of properties which might be expected to be different on either side of the equilibrium curve which separates the superconductive and the normal phases in H, *T* space These studies are based on the hope that clues to the nature of superconductivity might thus be found Unfortunately most of these investigations have produced negative results Thus there is no difference for the two phases in the x-ray diffraction pattern[38], in the photoelectric effect[39], in the absorption of β-particles[40] or of slow electrons[41], in the reflectivity of visible light[42], in the absorption of infra-red radiation[43], and in the transmission of visible and ultraviolet light[44] Furthermore, there appears to be no volume change accompanying the transition[45], nor do the elastic properties[46] or the thermal expansion coefficients change However, all the thermoelectric effects disappear below the transition temperature[47]. More recently, it has been confirmed[48] that a sharp change occurs in the thermoelectric force of tin about 0 2°K above the temperature at which the resistance transition occurs This suggests that intermediate electronic changes occur before superconductivity takes place, but this possibility has not received further substantiation Mechanical strain has been shown to have marked effects upon the superconductive properties of a metal. For example, it has been possible to raise the transition temperature of tin from 3 72°K to 9 00°K by the application of mechanical stress[49] Finally, the thermal conductivity[50] of a metal is distinctly different in the two states for temperatures less than the critical temperature, the data being such as to indicate that the free electrons are no longer able to take part in heat transport at temperatures well below the transition temperature

This review might well conclude with a brief description of what appears to be the first and, at present, only application of the phenomenon of superconductivity In 1938 D H ANDREWS[51] conceived the idea of using a superconductor, maintained in its transition range, as a detector of radiant energy Advantage may be taken of the very large value of the temperature coefficient of resistance in this range, which affords high sensitivity The low temperature of operation guarantees, further, rapid response in virtue of the low heat capacity and also a low ultimate limit of detectability because of the low level of noise due to statistical fluctuations Many bolometers[52], using niobium nitride as the sensitive element, have been studied, the emphasis on this type being placed for the reason that field operation is possible, since liquid nitrogen and hydrogen only are required A typical bolometer has a time constant of 5×10^{-4} sec, a noise level equivalent to 5×10^{-10} watt of incident radiation, and a minimum detectable energy in a single flash of 2×10^{-8} erg Recently[53], it has been demonstrated that the superconductive bolometer may be used as an alpha particle detector which not only counts the particles but also gives an indication of their energy

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Development and Application of High Vacuum Technique

M PIRANI, Ph D, F Inst P

THE conception of the application of high vacua to technical processes as unit operations is of modern date and is based on the notion that the best means for protecting materials and products to be processed *e g* by melting, evaporation, annealing, distillation *etc* consists of preventing reactions with the surrounding atmosphere by its complete removal

It is generally agreed that in speaking of high vacua we mean residual pressures of air or other permanent gases of the order of about 10^{-6} atm In terms of the kinetic gas theory there are then only $c\ 2\,5 \times 10^{13}$ gas molecules left in 1 cm^3 The pressure 10^{-6} atm can also be expressed as $0\,76 \times 10^{-3}$ mm Hg or 0 76µ In chemical distillation at low pressures, the vapour pressure of the distilled liquid may be of the order of a few millimetres of mercury (at 2 mm pressure $c\ 6\,5 \times 10^{16}$ molecules will be present in 1 cm^3), whereas the pressure of the residual permanent gases will be in the micron range

The fact that it is possible to reduce the permanent gas content of the container to the micron range implies that the container is 'tight', in other words that no air can leak in from the atmosphere, or alternatively that the amount of leak is negligible The nature of the process we carry out will define what may be called '*negligible*'

There is also a time factor to be considered, namely the time in which the system can be 'evacuated' to a certain ultimate pressure, and this governs the 'throughput' of each process In order to describe this magnitude we talk of the 'speed' of a vacuum system. The unit operation 'vacuum' is therefore governed by the magnitudes of *1* lowest ultimate pressure, *2* leak rate and *3* speed.

HISTORICAL DEVELOPMENT

The development of high vacuum techniques started from small beginnings about half a century ago, and especially rapid progress has been made within the last ten years. It is this latter period which will be reviewed in this article. It covers a comparatively short period, but the literature published in this particular field is so vast that no author will be able to quote more than a small part of it and this is bound to be biased by his personal experience. Having this in mind the reader may like to become acquainted with the subject by a tabular statement given in *Table I* which shows in a general way how vacuum equipment and physical and chemical methods using vacuum techniques have developed partly independently of their industrial applications.

During the early stages of this development, industrial applications of vacuum techniques made rapid progress, sometimes almost too rapid considering the state of vacuum art at that time.

This is certainly true of W. ROHN's vacuum melting furnace wherein the metallurgical, electrical and furnace developments were technically infinitely more advanced than those on the high vacuum side which were still in their infancy. This made it impossible to get the ultimate benefit of the high vacuum melting and casting technique.

In the first decade of this century, as a result of the absorption of physicists into industry, new methods, especially vacuum measuring methods, originated in industrial physics laboratories as a result of *ad hoc* investigations, often using the manufactured article itself as a measuring gadget, *e.g.* electronic valves. In the past decade, through the urgent need of certain industries which had to apply high vacua in their processes, vacuum equipment left the domain of the applied physics laboratory and became an industry in itself.

The development of high vacuum techniques as seen today may be said to date from the thorough study by W. GAEDE on the flow of gases at low pressures[8] which revealed that the width of ducts in a vacuum system plays a dominant role in the speed of evacuation. He calculated that for his molecular pump to have a speed of 2.8 ft³/min, tubes of 22 mm diameter would be necessary for a 3 ft duct.

However, it was another fifteen years before C. R. BURCH[9] again stressed the point that very much bigger ducts were now needed, when he published his classical experiments with oil vapour stream pumps. Only through the 1940 'Manhattan Project' in the U.S.A. did the use of really wide pipes and

Table I

Development of vacuum science techniques and equipment	*Period ending*	*Industrial applications*
MALIGNANI[1] introduces the first 'getter' by using an electric discharge in phosphorus vapour to scavenge residual gases Reciprocating and rotary pumps (*Fleuss Siemens-Pfeiffer*) Rotary mercury pumps (*Gaede Barr and Stroud*) Mercury manometers (*McLeod*) Melting of pure tantalum *in vacuo* with arc furnace[2] Pure tantalum metal filament made by dissociation of tantalum oxide *in vacuo* (*Bolton*)[3] High voltage gas discharge used for qualitative pressure measurements	1905	*Cooper Hewitt* mercury discharge lamps Carbon, osmium and tantalum vacuum lamps *Moore's* high voltage discharge tubes Tungsten filament lamp (extruded filament) Glass mercury rectifiers Production of melted tantalum at 0.01 mm pressure (100 gm batch) for lamp filaments and other applications Moderate vacuum x-ray tubes
Hot wire gauges (*Pirani Voege*) Tantalum made by dissociation of tantalum chlorides and subsequent melting *in vacuo*[4] Arc melting *in vacuo* with barium oxide activated cathode and 900 amp arc[5] Melting in concentrated electron beam[6] High purity vacuum melted iron (*Kreusler*) Dehydration of salts *in vacuo* (*Krafft*)[7] Use of ice sublimation *in vacuo* for the preservation of biological substances (*Shackell*)	1910	
Radiometer gauge (*Knudsen*) Beginning of mass spectrometry (*see Dechend* and *Hammer*) Molecular pump (*Gaede*) 2.8 ft³/min Diffusion pump (*Gaede*) 0.17 ft³/min Improved getters	1915	Drawn filament tungsten lamps First electronic tubes First mercury rectifiers in metal tanks, with rotary mercury pump attached High vacuum x-ray tubes (*Coolidge*)
Ionization gauge (*Buckley*) Study of electron emission from hot metals (*Langmuir*)	1920	Use of improved 'getters' in lamps Mains operated amalgam cold cathode Neon tubes Transmitting valves (up to 5 kw)
	1925	Mass production methods for electric lamps and electronic devices Metal melts of up to 4 tons *in vacuo* (*c.* 5 mm Hg (*Rohn*)
Improved molecular pumps (*Holweck*) 320 ft³/min Vacuum oil vapour stream pumps (*Burch*[9])	1930	Molecular distillation *in vacuo* (*Burch-Washburn*)
	1935	Gas discharge lamps for illumination High energy x-ray tubes
Cold cathode ionization gauge (*Penning*)	1940	Deep temperature dehydration
High speed oil vapour stream pumps up to 10,000 ft³/min Silicone oils Rapid measurement and control of leakage (*Nier et alia*[11]). Further improved molecular pumps (*Siegbahn*) Cold (radioactive) cathode ionization manometer (*Mellen*) Fore pumps made 'water vapour proof'		All metal industrial high vacuum plant (*e.g.* 1,000 ft³) Big valves, *e.g.* 16 in High vacuum metallurgy, 300 lb copper Metal deposition and lens blooming Booster pumps with maximum speed at given pressures

Table II. Speeds of Tubes of Various Lengths and at Various Pressures

Diam in	Speeds of conduits at 10^{-4} mm Length ft					Multiplying factor at given pressure				
	1	2	4	8	16	10^{-3}	10^{-2}	10^{-1}	1	10
0 5	2 2 (15*)	1 2 (9 5*)	0·6 (5 5*)	0 3	0 15	1	1 2	3 7	32	320
1	10 (63*)	5 5 (36*)	2 (25*)	1 5	0 75	1	1 4	6	55	550
2	70	40	22	11	5 5	1	2	12	110	1,100
4	400	250	140	80	40	1 01	3	21	210	2,100
6	1,200	800	500**	250	130	1 1	3 8	32**	320	3,200
12	7,000	4,500	3,000	1,800	1,000	1 4	7	62	620	6,200
16	15,000	10,000	6,300	4,000	2,200	1 6	9	85	850	8,500
24	35,000	26,000	19,000	12 000	7,000	1 9	13	130	1,300	13,000

valves (sealed and/or packless) become common practice[10, 11] *Figure 1* shows the principles of two common types of vapour stream pumps

Today a 10 inch oil vapour pump, having a speed of 8,000 ft³/min at 10^{-4} mm and provided with a 14 in valve, belongs to the standard vacuum equipment of many modern laboratories *Figure 2* shows some typical modern high vacuum equipment designed to evaporate metallic films on a mass production basis, on to such items as mirrors and car reflectors It has a chamber capacity of 50 ft³ and a 'system pumping speed' of about 3,000 ft³/min at 10^{-4} mm which permits evacuation and coating times as short as 20 minutes The chamber, one of the vapour stream pumps and the control unit are shown in the foreground

Table II gives 'speeds' (admittances) for different diameters between 0 5 and 24 in for tube lengths between 0 5 in and 16 ft and pressures[10] between 10^{-4} and 10 mm The left half of *Table II* gives the speed of conduits in micron ft³/min per micron pressure difference at 10^{-4} mm Thus the speed of a 6 in diameter conduit of length 4 ft is found to be 500 in the left hand half of *Table II* (it is marked**) and if the speed of this same conduit is required at 0 1 mm pressure then the factor given is 32 (right half of the *Table II*) which gives a value of 16,000 ft³/min The figures in brackets with an asterisk refer to lengths in inches instead of feet

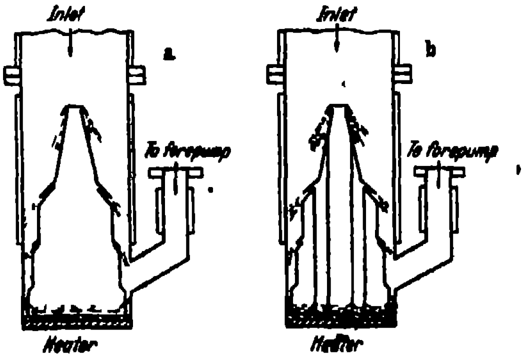


Figure 1 a *Metal vapour pump of the non-purifying type and* b *of the purifying type*

(*Courtesy Electronics, and G L Mellen*)

PRODUCTION OF HIGH VACUA

Limited space makes full discussion of the various methods for production of high vacua impossible, but excellent reviews already exist on this subject[11, 12, 13] Fore pumps covering the range from atmospheric pressure to about 0 05 mm are used in series with high vacuum pumps, which take over at 0 1 to 0 2 mm and reach 'fine pressures' of 10^{-3} mm. By careful adaptation of the two pumps at the 'take over' pressure, stability of the fine pressure against fluctuations of the forepressure is achieved

High vacuum pumps in the early days were mainly of the rotary type, but have nowadays been superseded by 'diffusion' pumps

Although one can state that the production of high vacua has ceased to be an art and has become a standard unit operation there are still a few practical problems to be solved One of them is the avoidance of back diffusion of permeable 'foggy' oil molecules[14] against the vapour stream in a diffusion pump without reducing the speed of a system considerably *e g* by cooled baffles[12]

The thirty year old controversy—diffuser *versus* ejector—has been settled by the investigations of P ALEXANDER and by D G AVERY and R. W WITTY[11] when they found that both the diffusion and the ejection (condensation) effects play their part in the functioning of a diffusion pump; thus E. N. DA C ANDRADE's designation 'vapour stream pump' which allows for both effects seems to be satisfactory[15]

The calculation of the 'speed' of a system including all the elements like pumps, freeze traps, valves, ducts *etc* has been extensively discussed in the literature[10, 11, 12, 16, 17] and no vacuum engineer should be at a loss about these principles

MEASUREMENT OF LOW PRESSURES

There are two types of instruments for the measurement of low pressures

1 those which measure the gas pressure directly *e g* by the height of a column of mercury or another liquid *e g* butylphthalate, compression manometers or molecular manometers and

2 those measuring an effect which is a function of the pressure (and sometimes additional factors) like the cooling of an electrically heated wire or the ionization caused by a source of electrons

Both groups are discussed authoritatively by S DUSHMAN[16] and R JAECKEL[47a]

The choice of a suitable instrument is influenced by the pressure range, required constancy, accuracy and reproducibility Often only the order of magnitude is required, but this already means a lot because nine to ten orders of magnitude have to be covered

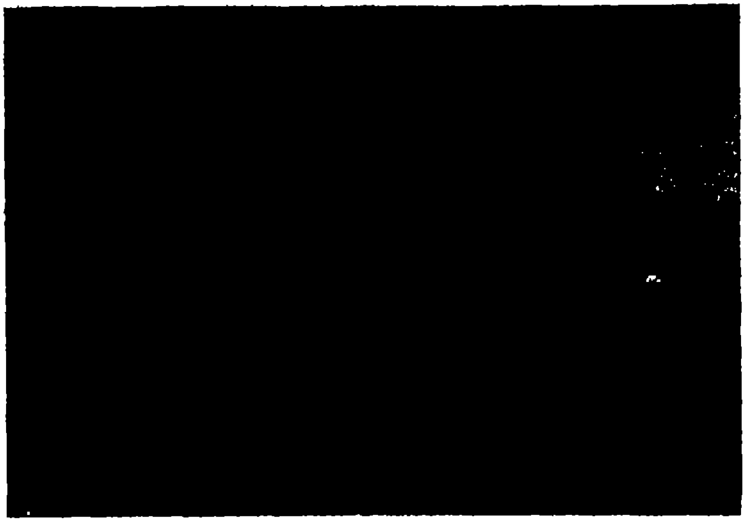
Table III

	Pressure range in mm
Mercury (and other liquid) manometers	10^{-3} to 2×10^{3}
Compression manometers (*e g* McLeod)	10^{-6} to 10^{1}
Bourdon gauge	10^{-1} to 2×10^{3}
Heat conductivity gauges	10^{-4} to 10^{1}*
Quartz fibre	10^{-4} to 10^{-1}
Quartz membrane	10^{-7} to 10^{-2}
Radiometer gauges	10^{-7} to 10^{-3}
Hot cathode ionization gauges	10^{-8} to 10^{-3}
Cold cathode ionization gauges	10^{-6} to 10^{-1}
Mass spectrometer	10^{-10} to 10^{-6}

* *The range may be extended up to 10^{3} mm if convection is used*[47a]

Table III shows the approximate ranges for different instruments used to measure low pressure

One interesting instrument worthy of special mention is the so-called 'Alphatron'. This is an ionization gauge in which a constant stream of ions is generated by alpha particles emanating from a small radium source which is packed in gold foil. Although the accuracy of this instrument is not higher than that of other ionization gauges it has the advantage of being easy to handle and covering a very wide range of pressures (it can be used from 10^{-3} mm up to 100 mm) This makes it especially useful to the chemical engineer who wants to cover a wide range of pressures with one instrument



(*Courtesy The Times Review of Industry*)

Figure 2 Industrial evaporator

It should be noted that the vapour pressures of oils used in modern vapour pumps are between 10^{-4} and 10^{-8} mm at 20°C[19, 20] and extreme care must be taken when measuring such pressures, particularly when using the hot cathode type of ionization gauge The measured pressure may then be anything from 20 to 200 times the actual pressure because of decomposition of the oil vapour molecules into lower hydrocarbon molecules

The condition that a vacuum apparatus is 'perfectly tight' is a necessary pre-requisite for the success of a process As the late pioneer of vacuum metallurgy W ROHN put it, about 1920, it is better to have a 'tight' apparatus at 1 mm pressure than a leaky apparatus at 1/100 mm pressure because of the cumulative contamination effect from air leaking in. As 'perfect' tightness cannot be achieved, the maximum permissible leak should be defined in every instance Its magnitude depends on the particular process and it should not be due to air penetrating from outside, this in turn is to be checked by observing the increase in pressure which is hyperbolic (asymptotic) when the increase in pressure is due to degassing and it is rectilinear when it is due to a real leak

The magnitude of a leak is often defined in 'micron cubic feet per hour'. This is a leak producing an increase of 1 μ/hr in 1 ft³ volume. Leaks can therefore be calculated by multiplying the rate of pressure rise in μ/hr by the volume of the vessel in ft^3 In μ/sec and l, this is equal to 8 × 10^{-3}μl/sec

There is, as a rule, the further condition, referring to 'economic throughput', that *e g* a 50 ft^3 tank should be pumped down to 10^{-4} mm in a given time *e g* ½ hr

The testing of components and assemblies of vacuum equipment has developed into a special art of dynamic vacuum testing techniques and has given rise to a few instruments of which the mass spectrometer is the most elaborate and perfect[11 12] In 'trivial' leak testing the sudden increase in ionization current of an ionization manometer or the jerk of the pointer of a hot wire manometer when an acetone spray, or a stream of town gas or hydrogen, is directed against the suspected place such as a weld, is a sufficient indication for the existence of a leak

APPLICATIONS OF HIGH VACUUM TECHNIQUE

With all these tools available many applications of high vacuum techniques made rapid progress during the past decade The main applications at present are the evaporation of metals and other substances *in vacuo*, vacuum dehydration, molecular distillation, melting, casting and sintering of metals and alloys *in vacuo* including annealing In all of them one of the main advantages is that perfect protection is obtained by the absence of an atmosphere

In mass production processes of the batch and continuous type, which often compete with each other, there is no general rule which is the more efficient One has to consider the minimum time required for degassing This will vary for different articles *e g* metal deposition on plastics or exhaustion of cathode ray tubes On the other hand the number of objects which can be processed simultaneously and the time cycle for loading, processing and unloading, and its influence on the expenses for labour have to be studied Finally the maintenance costs for different processes have to be compared

How these considerations may be affected by the different 'variables' of a process can be seen in the following two examples which are typical

VACUUM DEPOSITION

The deposition of metal and other substances on paper, resins and glass, is now an industrially established technique and is certainly going to displace rapidly the orthodox methods like spraying and chemical deposition, especially as big sizes are no obstacle and mass production (batch and continuous) is now a matter of course[13]. Even so, there are a few variables which have to be watched carefully, and the importance of these varies with the process. The variables concerned in deposition are

a temperature of vapour (as governed by temperature of source of vapour)

b temperature of target

c distance from target of object to be coated

d pressure and type of residual gas

e amount of vapour produced per second

f type of metal or alloy or other substance to be deposited

g state of surface of target (which in turn is influenced by its chemical composition and by the pre-treatment)

h application of a protective coating *e g* by silica and the post-treatment by temperature in a controlled atmosphere or by treatment with liquids

It is clear from this list that even a 'perfect' vacuum apparatus is no guarantee in itself for the success of the process if knowledge of the influence of any of the variables above is not adequate

Apart from the practical aspect there is also a scientific one while the 'art' of deposition has already reached a high state of perfection this is not so with fundamental knowledge and understanding of the deposition process The structure of the particles, the surface condition of the deposited metal *e g* aluminium which might have a molecular oxide film, their spacial arrangement, their mobility in a fresh deposit, the action of surface forces causing competition between adhesion and coalescence of the particles[14] (especially with 'thick' deposits over 1 μ), may still be subjects for fundamental research.

MOLECULAR DISTILLATION

It has long been recognized that in order to be able to distil substances which are liable to thermal dissociation, the distillation should be carried out *in vacuo* *i e* under such conditions that every molecule which leaves the evaporating surface reaches the condensing surface without impinging on gas molecules In order to attain this aim, the pressure of the permanent gases should be so low that the mean free path of the permanent gases (if only *they* were present) is greater than the distance between the condenser and the evaporator surface

As the vapour molecules behave more like 'fogs', collisions between vapour molecules of their own kind is not so objectionable and the actual vapour pressures may easily be a few orders of magnitude higher than the permanent gas pressure[14, 15, 16].

Apart from these pressure conditions which concern us especially in this review there are a few others which are not connected with vacua at all, but will drastically affect the efficiency of molecular stills Some of these are

1 heat transfer of a thin film formed on a glass or metal substance in a falling film still[27, 28]

2 wetting power of liquids for metal and glass surfaces

3 thickness of falling film and, if the liquid is going to be sprayed on to a surface, the heat transfer from spray particles to film

Only two of the interesting modern applications of molecular distillation will be mentioned, namely the study of film-forming materials for paints and the distillation of vitamins on a production basis (250 kg/hr)[6, 31]

MELTING OF METALS UNDER VACUUM

It is imperative to remove all gases in such processes as sintering, melting and casting of sensitive metals, especially those which form irreversible compounds with gases, like tantalum or titanium There is, therefore, only one satisfactory method and that is to evacuate the furnace in which the process is carried out

This was recognized long ago (1903) by BOLTON for tantalum, but it is only lately that the vacuum melting and casting of metals has become a unit operation, though so far it is only carried out on a moderate scale up to about 300 lb of metal It has mainly been applied to unorthodox metals like tantalum, zirconium and titanium[33, 34], but interesting and hopeful results have been obtained in the production of extra pure copper[7] and molybdenum[35]

Table IV

Degasing time hr	*Pouring pressure mm Hg*	*Oxygen* % × 10³	*Hydrogen* % × 10⁵
1	0.038	8.8	9
1	0.60	13.5	10
3	0.024	8.1	3.8
3	0.079	19	19
5	0.014	4.8	5
5	0.094	8.5	10

Table IV shows the effect of degasing time and pouring pressure on the gas content of copper ingots

Vacuum has been used in the promotion of such reactions in which vapour or a gas is developed *Table V* gives a list of such reactions and *Figure 3* shows the effect of temperature on the vapour pressure of a number of metals[7]

Though the vacuum and electrical parts[37, 38] of the equipment which is used for these purposes is quite well developed and as such would be able to cope with nearly all the metallurgical problems which arise in connection with it, there are quite a few questions which will have to be studied in more detail before there is a basis for industrial processes, one of them being the degasing of metals during casting by 'straining' thin layers *in vacuo*

There is also the casting technique itself to be further investigated if sound ingots are to be obtained because, as W ROHN has already pointed out, holes can easily develop by cooling and shrinkage effects when the outer shell solidifies before the inner core (Such holes might easily be attributed to gas evolution)

In the preparation of pure metals by vacuum treatment of compounds, the super-imposition of techniques *e g* chemical separation or galvanic deposition followed by vacuum refining, must be further studied[4]

The question as to when vacuum sintering is imperative and will give better results than sintering

Table V Vacuum Thermal Reductions which have been Investigated Recently

Metal	*Reaction*
Magnesium	$2(MgO\ CaO) + 1/6FeSi_6 \xrightarrow[0.005\text{ to }0.5\text{ mm Hg}]{1{,}100\text{ to }1{,}175°C} 2Mg \nearrow + 1/6Fe + 2CaO\ SiO_2$
,,	$3(MgO\ CaO) + 2Al \xrightarrow[0.005\text{ to }0.5\text{ mm Hg}]{1{,}050\text{ to }1{,}175°C} 3Mg \nearrow + 3CaO\ Al_2O_3$
Calcium	$6CaO + 2Al \xrightarrow[0.005\text{ to }0.1\text{ mm Hg}]{1{,}100\text{ to }1{,}175°C} 3Ca \nearrow + 3CaO\ Al_2O_3$
Lithium	$6LiOH + 4Al + 6CaO \xrightarrow[0.005\text{ to }0.1\text{ mm Hg}]{1{,}100\text{ to }1{,}175°C} 6Li \nearrow + 2(3CaO\ Al_2O_3) + 3H_2$
,,	Spodumene $[LiAl(SiO_3)_2] + Al \xrightarrow[0.005\text{ to }0.1\text{ mm Hg}]{1{,}050\text{ to }1{,}150°C} Li \nearrow$ + complex silicate
Barium	$4BaO + 2Al \xrightarrow[0.1\text{ mm Hg}]{1{,}050\text{ to }1{,}200°C} 3Ba \nearrow + BaO.Al_2O_3$
Niobium	$Nb_2O_5 + 5NbC \xrightarrow{\qquad\qquad} 7Nb + 5CO$

(Courtesy Chemistry and Industry, and R A Shaefer)

in a protective atmosphere is not finally settled This applies especially to the use of small quantities of residual gases like argon, neon, nitrogen, mercury or hydrogen, which might abbreviate the pumping time very appreciably and which are already being used occasionally during pouring in order to avoid the 'shrinkage holes' mentioned above

In sintering techniques the topo chemical conditions for the speed of reactions (as opposed to the equilibrium which is very rarely approached in technical processes) such as the degree of comminution of the re actant, characterizing its accessible surface, the degree of contact between particles, the porosity of the mix, have an important influence on the through-put This is especially true of such sintering reactions between solids as are governed by diffusion processes[39]

DEHYDRATION

In the drying of sensitive materials the evaporation of the mixture is done at low temperatures The materials are pre-frozen (STOKES) and the water vapour is removed at free air pressures of the order of 10 to 100 μ The moving force in this process is obtained by putting a cold trap having a surface temperature of about — 60 to — 70°C between the pump and the cabinet in which are placed the substances which are to be dried[39, 40 44]

Where cheap steam is available a multi-stage ejector may provide the driving force A four-stage ejector will be suitable for producing pressures down to 0 5 mm and will have a capacity of 200 ft³ min of entrained air with 200 lb of steam per hour at 4 atm (gauge)

Vacuum drying at medium temperatures e g 15 to 30°C, is used on an industrial scale in the U.S A for orange juice concentration. Plant processing over 20,000 l/hr of orange juice and concentrating it to one fifth its original volume has been operated since 1944 by the Vacuum Foods Corporation in Plymouth, Florida[44] (now Minute Maid Corp) A pilot plant processing a few thousand pounds of coffee powder per month has been erected by the National Research Corp in Boston, Mass, and will be expanded into a larger plant next year.

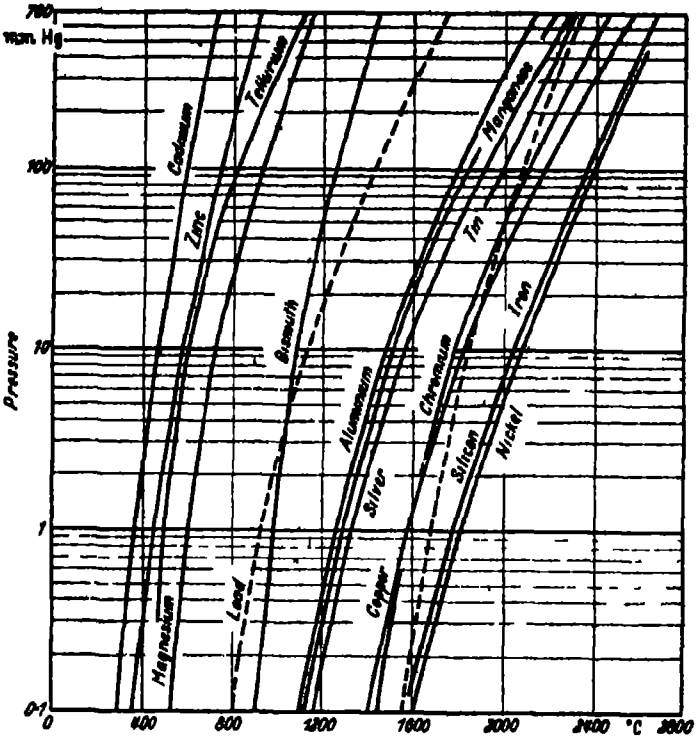


Figure 9 *Effect of temperature on vapour pressure of various metals (data of K K Kelly)*

(Courtesy Chemistry and Industry, and R A Stauffer)

The problems in drying at low temperatures by using a refrigerated condenser are not so much vacuum problems as heat transfer problems, because the ice crust which is formed when water vapour is deposited on the cold trap has a low heat conductivity. Rotary condensers with ice scrapers are one answer to this problem[43]

Vacuum drying from the frozen state has another interesting aspect By preventing the mobility of the molecules they remain in the same place as they were in the liquid, hence they do not coalesce and therefore the powder after drying has a very large surface This means that it will have a high solubility, while if the drying had taken place in the normal way by application of heat, coalescence[46] of the particles would have taken place and the result would have been a substance with a small accessible surface and smaller solubility

If we hold the summary of present achievements discussed above against the list of desiderata, we are probably entitled to say that in modern vacuum engineering the stage has now been reached where the prevailing practical problems can be dealt with adequately. However, permanent close collaboration between engineers and scientists has to continue. There is wide scope for fundamental studies in order to strengthen the scientific foundations of the vacuum technique

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Water Erosion : Development of the Present Approach to the Problem

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SOIL conservation services have in most places been initiated as a result of the considerable loss of soil caused by water erosion Early work was, therefore, concerned largely either with reclamation or with the removal of immediate threat of catastrophe H H BENNETT[1] records that in the initial stages of his work, in the early 1930s, he had doubts 'whether or not it was too late, or whether we could go fast enough to catch up with the job that confronted the Nation'. This statement could no doubt have been made in most of the affected countries at a similar stage in the development of their soil conservation services Thus speed was imperative, and in such circumstances it was inevitable that the first measures applied were characteristically trial, and error in nature rather than application of the results of research

Two things soon became apparent. These were, first that the available hydrological information needed appreciable modification, and secondly that only rarely is one single practice by itself successful in the control or appreciable mitigation of erosion For example, in the early stages there was little information on which to base decisions with regard to spacing of terraces, gradients, lengths of pondage banks, and the like For some years the urgency of remedial works dominated and experience rather than experiment continued to be relied upon, and whilst very definite advances were made these resulted from observations rather than from long range, soundly conducted investigations Thus the early information on the subject is to be found for the most part in more or less general accounts of works carried out on various practical projects

H H BENNETT[2] in 1939 gave a very comprehensive statement of the problem and the combative measures known at that time, but as that author then recorded there was a serious deficiency of information on many of the diverse factors involved These factors are essentially of two types—those with a strong engineering bias and those of largely or wholly agricultural nature

As reclamation formed such a large part of the first intensive campaign against water erosion it was the engineer who was called upon in large measure to handle the work and the agriculturist at best was perforce required to adopt the role of engineer Unfortunately the dominance of the engineering approach continued far beyond the stage of reclamation and can still be seen today in the attitudes of farmers and all too many others, not excluding scientific agricultural workers Even where an analysis quickly shows that the fundamental cause is some agricultural malpractice, the stress is often still laid on the engineering aspects and there is considerable reluctance to adopt that approach outlined by G V JACKS[3] which follows on a realistic and sound examination of the basic factors involved

The problem of water erosion may be said to be caused by water attaining scouring velocity and thus an obvious solution is to so control the flow that this does not occur Control of flow may be achieved in a number of ways, one of which is to lead the water off the land at low velocity and dispose of it safely into stabilized waterways and permanent water courses This is, of course, an engineering approach Agriculturally, however, any solution which merely takes water safely off the land is incomplete and unacceptable since crop production demands primarily that, up to a point, the maximum amount of water be stored and retained in the soil for future use The work of the engineer and the agriculturist seems thus to be related and as the work of soil conservationists proceeded the necessity for such correlation became more and more evident The relationship is well shown by M L. NICHOLS[4] who, writing as an engineer, still has much more to say on biological aspects than on engineering ones, whilst J D LONG[5] refers to agricultural engineering as the branch of engineering closest to biology

Water erosion in many countries, particularly in the New World, has proceeded to such a degree and over such huge areas that for a long time to come reclamation work on a large scale must continue, but if this phase is not to be permanently the dominant feature of soil conservation activities prevention must receive increasing attention Above all the experience of the past thirty years shows that the farmer needs to be educated to the fact that water erosion is not something to be accepted as inevitable and to be subsequently retrieved by the engineer He must learn that water does not erode soil simply because the slope of the land exceeds some empirical critical gradient but rather that, in the main, the loss follows some agricultural malpractice which preconditions the soil so that it is incapable of readily absorbing rainfall or of withstanding the force of excessive run-off water It is to be stressed that the condition of the soil profoundly influences the amount of run off and, through both this and the intrinsic physical structure of the soil, the scouring potential of that run-off

In arriving at this stage the work of W D ELLISON[6] [10] has been an outstanding contribution to the overall knowledge of the subject The causes of water erosion can be stated in general terms in several ways But these general statements, however true for individual areas, are dangerous in so far as they may be accepted by the farmer as providing the basis for combative measures It is essential that the problem be stated in precise terms applicable wherever the problem arises This is what Ellison's work in a large measure succeeds in doing and the inescapable need for the combination of several sciences is clear Thus the studies of infiltration capacities[6], physical in essence, are none the less inseparable from agricultural status and practice both as studies and in their application Ellison's contributions can scarcely be adequately dealt with other than comprehensively but particular attention might be called to those parts dealing with infiltration[6] and with soil transportation by surface flow[10] From work of this nature it is clear that the basic cause of water-erosion is to be found in the structure of the soil and therefore all those treatments which influence this structure have bearing on the problem This being so, research on many aspects of cropping and soil tillage are of direct consequence to the soil conservationist and the search for more suitable grasses by the agrostologist, the study of drought resistance by the physiologist, and the investigation of fertility by the soil technologist are at least as important as effects of raindrop impact, waterway design and scouring velocities of run-off water

That water erosion has over the past thirty years assumed the prominent place in agricultural thought that it now occupies is largely due to development of power farming machinery This mechanization has acted in several directions which have tended to accelerate erosion Steeper slopes have been brought into cultivation, land has been worked more quickly after rains than was possible with horse-drawn implements, thus allowing less growth of soil binding and holding weeds and grasses, whilst the reduction in, or even elimination of, farm animals has resulted in the return of less animal products to the soil and a decline in the amount of ley farming

Soil loss may be either spectacular as in gullying or insidious as in sheet erosion but in each case the factors which precondition the soil are much the same, with loss of structure predominating One of the earliest contributions on this aspect was that by H E MIDDLETON[14] in which attention was directed to organic matter and colloid content of the soil in a comparison of erosive and non-erosive types

The investigations of soil structure are involved and there are still many gaps in our knowledge For the worker on soil conservation, either physical or biological, the contribution of J B PETERSON[15] is worthy of particular note since it provides a basis from which further investigations on several aspects of soil erosion might be commenced Other contributions of similar character to which attention might be drawn are those by L D BAVER[16] and A M O'NEAL[17]

Both the deterioration in structure and the exposure of the soil denuded of effective vegetative cover have undoubtedly been accelerated by farm mechanization Literature abounds on this subject, particularly from the United States where virtually every agricultural region has been adversely affected Serious study of the problem quickly revealed that whatever various specific measures might be required from place to place, field to field, or country to country, the basic requirement was sound farming practice The need to return to rotational farming was soon apparent as also was the necessity for devoting each class of land and soil to the purpose for which it was most suited Farm planning, as developed by the United States Soil Conservation Service, was a logical outcome.

Since the impounding of water in the soil both for use by the plant and to reduce run-off is of basic importance, investigations into improved methods of infiltration are of particular moment and in this regard the work of F L DULEY and L L KELLY[18] calls for special note From this type of work has developed the conception of stubble mulch farming, as described by F L DULEY and J C RUSSELL[19], and there seems little doubt that where suitable machinery for the conditions can be developed this practice with its sub-surface tillage will be of first importance in erosion control

The role of grasses in relation to soil structure and water intake is now receiving increasing attention and work such as that by F L DULEY and C E DOMINGO[20] and W S MARTIN[21] is of particular value to the soil conservationist Apart from their place in rotations, grasses are important to the conservationist in the uses to which they can be put for arresting or spreading water as on catchments and at waterway outlets, in the stabilization of waterways and other auxiliary earth structures, and thus much of the work of agrostologists is of considerable value in soil conservation

The utilization of grasses to combat water erosion quickly forces consideration of economic aspects as does the whole subject of land use Correct land use must, of course, be based on sound economics but long term economy, particularly from the national point of view, is by no means strictly or even positively correlated with immediate profit taking by the individual farmer Further, the individual farmer has normally not only learnt his farming in a particular restricted area, but has inherited, or acquired from his immediate life long environment, his whole outlook on what to grow, where to grow it, and to some extent how to grow it R SCHICKALE, J P HUMMEL and R M HURD[22] as the result of an economic study on certain aspects of erosion control stated that there was conclusive evidence that in the erosive sections of the Corn Belt soil conditions no longer warranted a highly specialized corn-hog type of farming The translation of that type of conclusion into appropriate change is a formidable task, but it is one which must continually confront the soil conservationist One of the greatest difficulties is to show the farmer that the proposed changes, made mandatory if his soil (*i e* his capital) is to be preserved, are immediately economically sound It calls for searching investigations by the agriculturist and the economist in collaboration as exemplified in the investigation reported upon by A C BUNCE and G W COLLIER[23]

One aspect of water erosion not of purely agricultural nature which is of very considerable importance to the farmer is the siltation of streams and reservoirs Frequently the basic cause of such siltation lies in the abuse of watershed lands and is thus remedied only when correct land use is effected In this matter a community-wide approach to the problem is generally called for so that the plans for all farms in one watershed may be integrated and the work implemented in the most effective way The relation of these matters to erosion as it directly affects the farmer is well covered in such publications as those of S C Happ, G Ritterhouse and G C Dobson[24] and C. B Brown[25]

Since the turn of the century the menace of water erosion of agricultural lands has heightened and it is fortunate that the will and ability to combat it have likewise increased In the first phase of intensive action land reclamation was the dominant motive, but as information was gathered it became obvious that all aspects of farming and land usage were involved To review the whole field of relevant research would be to cover much of the agricultural investigations for a very long time as well as certain aspects of hydrologic engineering for the past quarter of a century

No such attempt has been or could be made here, as would be made very apparent by reference to such papers as those by R E Uhland[26], F L Duley and O R Mathews[27] and C. E Ramser[28]

Probably the greatest advance of the past twenty years is in the method of attacking the problem One point appeals as being of outstanding significance This is that there has been marked departure from the previously all too frequent approach to soil problems of altering farming practices, crop plant varieties and so on to compensate for changes in the soil Obviously now there is an increasing emphasis on the necessity for so handling the soil that the deterioration does not occur or at least is appreciably delayed and minimized

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Chemistry of Specific, Selective and Sensitive Reactions

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A full understanding and the further development of the analytical methodology, which utilizes chemical reactions, demand primarily a scientific treatment of the following questions what is the basis and how does one arrive at methods of detection and determination that are characteristic of a material or a small number of materials, and that make it possible to handle successfully minute amounts of substance? These are the factors which are designated as the specificity, selectivity and sensitivity of analytical methods and the reactions that underly them

The present state of chemical knowledge will not provide precise answers to all parts of these questions, especially if only physicochemical laws are taken into consideration Nevertheless, pure empiricism does not offer the only solution to this difficulty Points of reference and guiding principles are available for handling these problems, which can be approached from different sides In the first place it is necessary to consider in detail the chemism of known unequivocal and sensitive reactions Efforts must be made to secure a clear understanding of the relations between the composition and constitution of reactants and reaction products, as well as of the relation of the particular type of reaction to the phenomena which are the bases of an analytical employment solubility, volatility, colour, fluorescence *etc* A further requirement is an extensive knowledge of all the factors that may influence the certainty and sensitivity of reactions in a positive or negative direction Finally it is necessary to include a consideration of such phenomena, which—though they cannot be directly utilized for analytical procedures—are model instances of processes, that play a role in analytical procedures Pertinent material is obviously to be sought in studies dealing with other fields of chemistry as well as with analysis, not neglecting publications that may have appeared many years ago The purpose will not be served by consulting abstracts , the original papers must be explored, because important statements often occur in seemingly incidental remarks or even in footnotes Frequently it is the interpretation of certain data by the author of a paper, or by authors in later papers, which leads to interesting conclusions Valuable leads often come from publications not dealing with analytical studies On the other hand, analytical papers frequently contain experimental results, the importance of which for other branches of chemistry, including even chemical technology, may far exceed the analytical interest Therefore, a sifting of the chemical literature, guided by the question as to the reasons for the selectivity, specificity and sensitivity of analytical procedures, brings to light a mass of experimental facts and data If these are arranged, classified, critically evaluated and supplemented, a province will be opened which by no means pertains exclusively to analytical chemistry It is rather an area of experimental chemistry, closely related to many special fields of chemistry , the term chemistry of specific selective and sensitive (s s s) reactions is an appropriate and justifiable designation for this branch of the science

The functional field of chemistry of s s s reactions, as just outlined, has grown out of recent tendencies and problems, which have confronted chemical analysis with new tasks These tendencies are rationalization of chemical tests through the greatest possible economy in material, time and labour The new problems were occasioned by more rigid demands regarding the purity of chemicals, and by the appreciation of the fact that small amounts of materials, which are associated with major quantities of other substances, frequently are so very significant in fixing the properties of technical materials, or in geochemical questions and also in biochemical processes, that their detection and determination becomes of primary importance. Spot test analysis offers distinct advantages in efforts to simplify analytical procedures and reach microchemical goals[1] By means of spot tests [2,3] by a simple macro technique, it often is possible, without preliminary separations, to carry out detections and colorimetric determinations (spot colorimetry) which are microchemical in their detection limits This success demonstrated that the decisive factor in *microanalysis is not the employment* of a particular technique but rather the ability to deal effectively with minute quantities of substances Of farther reaching significance, however, was the fact that spot test analysis has opened a new approach, which is characterized by an unprecedented variety in the choice and use of reactions. This has provided a vigorous impulse for research on the analytical utilization of reactions For such research the chemistry of s s s reactions has become a donor and an acceptor, as the following will illustrate

REACTIONS LEADING TO METALLO-ORGANIC COMPOUNDS

Organic compounds, which are capable of forming salts and also of participating in addition and condensation reactions, provide valuable subjects for studies of the analytical usefulness of reactions Previous experience has proved that definite atomic groups are responsible for the ability of organic compounds to enter into certain reactions, as well as for the colour, solubility, fluorescence *etc* of reagents and reaction products The activity of such groups however is not independent of the remainder of the molecule Other atoms and groups may exert an influence on the colour quality and solubility of reaction products Numerous observations on this subject are available[4], and they point to the existence of certain rules and regularities, which have led to the discovery of new organic reagents Studies of group action, which often require that due attention be given to the isomerism, tautomerism and resonance of organic compounds, have practical as well as theoretical value, since the introduction of reactive groups into organic compounds quite often results in reagents with desired effects Preparative organic chemistry may also benefit from such endeavours, because the synthesis of new compounds with a view to testing their analytical behaviour can result in improvements of the methods for preparing previously known compounds The principle of group action for the discovery of new tests has likewise proved useful in organic analysis

The important role of organic reagents in modern methods of inorganic analysis has fittingly been recognized by the recent publication of excellent monographs[5] However, an examination of these volumes reveals that the chemical basis of the applications of all organic reagents is by no means known, nor has their action been correctly interpreted in many instances. Much interesting research remains to be done here. The recording of the composition, constitution and properties of reaction products of organic compounds that have been turned to analytical use—a task that abstract journals for the most part perform inadequately—is of importance to the chemistry of complex compounds. Many new metallo-organic compounds, which can be fitted into certain classes of complex compounds, have been isolated in the course of analytical researches. The systematics of complex compounds has thus been enriched, but in addition members of totally new classes of complex compounds have been discovered in this way. Examples include the bi-nuclear compounds of palladous chloride with fuchsine hydrochloride isolated by P. W. West[4], which throw a light on the constitution of the previously described addition compounds of benzidine with metal salts, and also the compound of mercuric fluoride with benzidine hydrofluoride, discovered by C. Pertusi[5] in connection with a specific test for fluoride. The analytical study of complex-forming organic compounds sometimes discloses unexpected reaction products or reaction paths. Pertinent examples are salicylaldehyde (mode of reaction interpreted by P. Pfeiffer and his co-workers[6] has recently been put to analytical use by F. R. Duke[7]), the mercury- and silver-bearing compound of 8-hydroxyquinoline (oxine) isolated by R. Berg[8], the precipitation of palladium by means of 6-nitroquinoline, recommended by S. C. Ogburn and A. H. Riesmeier[9], the compounds of palladium salts with furfuraldoxime studied by J. R. Hayes and G. C. Chandlee[10], the production of inner complex salts of tervalent thallium recently discovered by F. Feigl[11], and the demonstration of the acidic character of inner complex palladium dimethyiglyoximate[12]. In such cases the question arises as to whether the structure of reaction products or the mechanism of their formation is not of more interest than analytical applications[13].

Papers on analytical chemistry have made chemists aware of numerous new inner complex salts the characteristics of which can now be critically examined. Even at this stage it may be stated that the previous characterization of these compounds by abnormally low water solubility and ready solubility in organic liquids as well as by abnormal colour intensity constitutes an undue generalization which needs revision[14]. The solubility of inner complex compounds in organic liquids, which makes possible their extraction in certain analytical procedures, appears to be dependent on group actions. However, evidence supporting this viewpoint is not available as yet, though it could be secured from quantitative solubility determinations. Such data would have great value in deepening the knowledge not only of inner complex binding but also in securing a better understanding of solution processes. There are still other problems where consideration and study is stimulated by inner complex compounds. Thus the formation and acid resistance of certain inner complex compounds point to the existence of so-called false equilibria (analogous to the familiar behaviour of cobalt sulphide and nickel sulphide), and there is also evidence, as in the behaviour of inner complex palladium compounds toward alkali cyanide, that sometimes false equilibria appear[15]. Furthermore, the surface and fusion reactions undergone by inner complex-forming organic compounds with solids are of many sided interest[16]. The instances cited here are indicative of the host of phenomena and problems that arise when, as demanded by the chemistry of s.s.s. reactions, organic reagents are considered not solely from the standpoint of their analytical utility, but when efforts are made to take into account all of the factors, which contribute to this usefulness.

CATALYSIS REACTIONS

New and better methods of detection and determination do not come solely through the use of organic precipitants and colour reagents. These goals can be reached by still other means. Catalysis reactions, the microchemical importance of which was revealed by spot test analysis, come first in this category. A familiar feature of the catalytic acceleration of reactions is that frequently the action is produced by very small amounts of material and is limited to quite definite reaction systems. However, these features simply signify sensitivity and selectivity. Actually, a considerable number of substances may be detected, or in some cases even determined, in minimal quantities with great selectivity by means of their catalytic activity in homogeneous and heterogeneous reaction systems. Many new catalytic effects have been discovered through analytical studies, and numerous catalysis reactions which had been forgotten have now become popular because of their use in analysis. This was the case for instance with F. Raschig's observation[17] in 1915 that alkali sulphide or thiosulphate markedly accelerates the reaction

$$2NaN_3 + I_2 \rightarrow 2NaI + 3N_2$$

which proceeds at an immeasurably slow rate in the absence of a catalyst. Much later it was shown[18] that the initiation of the iodine-azide reaction, which can be readily observed because of the evolution of nitrogen, can be used in the form of a spot test to detect inorganic and organic sulphides.

The following example illustrates a point of view characteristic of the chemistry of s.s.s. reactions.

R KEMPF[19] observed that the activation of persulphuric acid by Ag^+ ions, originally discovered by H MARSHALL[20], also applies to oxalic acid The latter is oxidized to carbon dioxide and water , and this fact is the basis of a volumetric method of determining persulphates The question arises at once whether this behaviour is characteristic of oxalic acid only. Although Kempf had found that many other organic compounds are oxidized by this reagent, this fact had not been stated in the analytical abstract because it was not of immediate practical significance Consequently, some forty years passed before F OBERHAUSER and his collaborators[21] explored the possibilities and discovered that it is feasible to determine the carbon content of certain water-soluble organic compounds by a wet method through the activated persulphate oxidation Recently it was shown that activated persulphuric acid readily decomposes many organic compounds or salts of organic acids or bases dissolved or suspended in water, and analytical use has been made of this finding[22] Another related effect is important to the chemistry of s s s reactions M DITTRICH and H BOLLENBACH[23] observed that, in the presence of Ag^+ ions, persulphate quantitatively converts silver iodide into silver iodate This observation has no analytical value as yet, but it merits considerable interest as an instructive instance of the reactivity of solids

FLUORESCENCE EFFECTS

The original application of this type of analysis was limited to the detection of fluorescing substances in a given sample, but has undergone a remarkable extension because of spot test analysis It was observed that reactions between two organic reactants, neither of them fluorescent, sometimes produce fluorescent compounds This makes possible sensitive spot tests for certain groups and organic compounds[24] For a long time, little attention was paid in inorganic analysis to the production of fluorescing compounds, although eighty years previously F GOPPELSROEDER[25] and M JAFFE[26] had discovered the fluorescence reactions of aluminium with morin and of zinc with urobilin These were clear examples indicating that selectivity and sensitivity could be combined in fluorescence reactions, analogous to these similar characteristics of catalysis reactions Stimulated by the studies of H GOTO[27] and C E WHITE[28], deserved attention is now being given to the production of fluorescing inorganic-organic compounds and to the quenching of fluorescence by means of certain chemical reactions. A contributing factor is that fluorescence can be employed not only for qualitative tests, but quantitative determinations based on photometric measurements of the intensity of fluorescent solutions are quite feasible. White suggested the term fluorometric analysis[29] for the use of fluorescence reactions in analysis Redox reactions, which lead to fluorescing compounds, also belong to this category Excellent examples are the interesting tests for oxygen and ozone by means of adrenaline and dihydroacridine discovered by M A KONSTANTINOWA-SHLEZINGER[30] and the specific test for tryptophane with perchloric acid described by H TAUBER[31]

When the fluorescence of compounds with organic components is considered within the framework of s s s reactions, it must be noted that atomic groups and linkages i e constitutive problems, play a part As yet the knowledge of these factors is too scanty to provide guiding principles which might facilitate the search for organic fluorescence reagents, as is the case when seeking new precipitation and colour reagents In this connection it is well to remember some observations that were made in analytically oriented studies and which demonstrated that the fluorescence of inorganic-organic compounds may also depend on their state of aggregation For example, many oxinates fluoresce intensely both in the solid state and when dissolved in organic liquids, whereas salts of oxine with inorganic and organic acids fluoresce only as solids, but not in aqueous solution[32] C E WHITE and M H NEUSTADT[33] made the interesting discovery that fluorescence appears in the system alkali zincato-benzoin only when magnesium hydroxide is present This indicates that the latter functions as adsorbent for a soluble zinc-benzoin compound, and thereby becomes responsible for the characteristic fluorescence, which constitutes this selective test for zinc It thus seems likely that the passage of dissolved materials into the solid or adsorbed condition may involve such changes in constitution as can result in fluorescence

The use of organic reagents, catalysis reactions and fluorescence reactions shows that taking specificity, selectivity and sensitivity as objectives has led to the abandonment of a one-sided preferment of certain types of reactions Hence it may be anticipated that photoreactions and chemiluminescence, phenomena which hitherto have been somewhat neglected, will likewise contribute to the solution of analytical problems Indeed, even reaction anomalies need by no means be merely undesirable effects , occasionally they too can be used to advantage by the analyst For example, a spot test for native albumen with tetrabromphenolphthalein ester is based on a so-called protein error[34].

CAPILLARY ANALYSIS AND CHROMATOGRAPHY

If the tests and methods of determination which were described within a particular period of years are arranged according to sensitivity and reliability, it becomes evident that it is much easier to find sensitive reactions than such as are selective or even specific Consequently it is necessary to take into account all possibilities through which the selectivity of reactions can be increased One possibility, which may be characterized as the removal of materials from a common reaction site, is based on observations that reach back a long way, and the significance of which became apparent only with the development of microanalysis F SCHÖNBEIN[35] was the first to discover that when solutions ascend strips of filter paper, or when drops of a solution spread in filter paper, the dissolved materials lag behind the solvent in separate zones Accordingly, local accumulations of materials result F GOPPELSROEDER[36], who made an intensive study of this zone formation, and who appreciated the value of this phenomenon for the separation and accumulation of dissolved materials and for the characterization of solvents, coined the term capillary analysis In spot test analysis frequent use is made of this zonal segregation of materials when carrying out drop reactions on pure filter paper or on paper impregnated with suitable reagents, because in this way it is possible to secure a better visibility of small quantities of coloured materials, and also to detect fractionated precipitations It is now known that capillary analysis does not depend solely on capillary spreading and the difference in diffusion rates of dissolved materials Filter paper is not merely a capillary medium, it acts at the same time as an adsorption medium by reason of the great area and chemical nature of the traversed capillaries and also because of the small but not negligible content of mineral constituents, which are highly dispersed throughout the paper The effects utilized by Schönbein and Goppelsroeder also appear with other materials which permit a capillary migration and adsorption of dissolved substances This fact was first appreciated by M TSWETT[37], whose studies on column adsorption, though overlooked for years, have made him the originator of chromatography[38], which is now widely employed [Studies of the chemistry of s s s reactions lead not only to the establishment of facts which cannot be found in abstracts, but occasionally also to interesting statements regarding priority Thus it seems not to be known that L REED[39], thirteen years before Tswett, discovered that it is possible to separate certain inorganic and organic salts (alkaloids) by column adsorption (on kaolin) Since Reed discussed both column adsorption and capillary spreading in paper, there is no doubt that the researches of Schönbein and Goppelsroeder served as the starting point for the development of chromatographic analysis. With no intent to disparage Tswett's importance, Reed's contributions cannot be overlooked.] The filter strip method has recently been revived and improved under the name paper chromatography by R. CONSDEN and co-workers[40]. This kind of chromatography is of considerable importance for the solution of microchemical problems Adsorptive separation is the result of selective addition or exchange reactions on the surface of the material serving as adsorbent Solution components are thus fixed in distinct zones of the adsorbent, where they then can be definitely detected by means of non-selective though sensitive reactions

MASKING AND DEMASKING

Important procedures for enhancing the selective action of reagents are based on the prevention of reactions If a selective reagent is undergoing several analogous reactions, the equilibrium positions of which at practically complete reaction are dependent on *p*H to different extents, adjustment of the reaction *milieu* to certain *p*H values or intervals can then prevent the occurrence of unwanted reactions This stratagem is used especially with organic reagents Another type of reaction impedance consists in lowering the concentration of ionic or molecular species without dilution so that certain colour or precipitation reactions no longer occur This is possible when the addition of appropriate reagents produces compounds where the reactions are of different types This procedure is known as masking By combination with *p*H adjustment, masking can frequently be employed to elevate the action of less selective precipitation and colour reagents to high selectivity or sometimes even to specificity Masking agents may be either inorganic or organic in nature In the latter case, the action of certain groups plays a significant role in the same manner as with precipitation and colour reagents

Because of their great practical importance and variety, masking reactions must be considered at considerable length in the chemistry of s s s reactions It has been found that undue generalizations must be avoided and new viewpoints taken into account Thus masking has hitherto been absolutely identified with complex formation, because the action of most masking reagents is due to the production of soluble complex compounds This identification is not correct On the one hand, there are numerous complex compounds where solutions show no masking effects, on the other hand, examples can be cited in which the production of soluble principal valence compounds may lead to masking This latter category includes the annulment of the basic action of NH_2– groups in carboxylic acids by the addition of formaldehyde (Sørensen formol titration[41]), the masking of the iodometric oxidation of sulphites by formaldehyde[42] as well as the masking of almost all reactions of molybdenum, tungsten and vanadium acids by hydrogen peroxide[43] or fluorides[44].

For the major part, masking reactions which occur in solutions and lead to soluble compounds are equilibrium reactions They usually require the use of an excess of the masking agent and can be reversed again by removal of the masking agent The freeing of previously masked ionic or molecular species has been called demasking[45] This merits consideration in regard to its use in analysis Pertinent instances are the demasking of $Ni(CN)_4^{-2}$ ions to Ni^{+2} ions by formaldehyde, and the demasking of dimethylglyoxime from $[PdD_2]^{-2}$ ions by cyanides These liberations are the basis of sensitive and selective tests for and determinations of nickel[46] and cyanide[47] Masking never completely removes certain ionic or molecular species, but only reduces their concentrations The extent of this lowering determines which colour or precipitation reactions can be prevented It is therefore easy to see that masked reaction systems can also function as reagents at times (*e g* Fehling's solution, Nessler's reagent)

If masking is defined as the lowering of an ionic or molecular concentration because of formation of principal or auxiliary valence compounds with the masking reagent, it is not necessary that the reaction products remain in solution Insoluble reaction products may likewise be masked against chemical reactions Thus a neutral or acetic acid solution containing iron and cobalt reacts with α-nitroso-β-naphthol to give a red-brown precipitate of the corresponding nitrosonaphtholates If, however, ferric phosphate and cobalt phosphate are precipitated by means of an alkali phosphate before adding the organic reagent, only the cobalt phosphate reacts with the naphthol In this way, it is possible to make a delicate spot test for cobalt in the presence of considerable quantities of iron[48] Analogous differences in the reactivity of the components of mixed precipitates are frequently utilized in spot test analysis. It may be assumed in such cases that the solubility of a non-reacting precipitate is too slight to furnish the ion concentration requisite to the occurrence of the particular reaction This corresponds to a reaction masking by precipitation There is still another type of masking which is related to the foregoing One constituent of a mixed precipitate may suffer the loss of much of its reactivity This is seen in the systems barium sulphate-lead sulphate, barium sulphate-calcium sulphate and with many mixed sulphide precipitates[49]. In such cases one solid seems to serve as a masking agent for another The same holds for certain insoluble complex compounds, where components when alone act as solid bases. For instance, in dolomite $CaMg(CO_3)_2$, the magnesium carbonate is masked against certain colour reagents, which promptly react with free magnesium carbonate (differentiation of dolomite and magnesite[50]) A water-soluble compound built into a crystal lattice of a solid may also be masked This is shown by H WOHLERS' observation[51] that barium sulphate precipitated from a solution containing potassium permanganate is deep red, and that the retained permanganate cannot be removed either by washing with water or by treatment with a reducing agent Wohlers' discovery was later developed[52] into a method for making small quantities of barium sulphate visible, a nice example of a useful idea derived from non-analytical studies.

TOPOCHEMICAL REACTIONS

The phenomena, which V KOHLSCHÜTTER named genetic formation of materials and topochemical reactions, constitute interesting chapters in the chemistry of s s s reactions The former term denotes the attribution of chemical and physical properties of a material to the particular conditions that prevailed during its formation If a particular reaction locale plays a role in determining the speed of a reaction as well as the permanent or transient retention of a reaction product and its properties, then a reaction becomes topochemical Important factors attending the formation of solid phases are the production of nuclei and the growth of nuclei, the speeds determining the form-species of precipitates F L HAHN's method[53] of precipitation from extreme dilution (which can also be accomplished by means of soluble complex compounds) enables the analyst to reduce the production of nuclei and thus to obtain, in place of gelatinous masses, dense precipitates, which filter well and are less prone to exhibit adsorptive properties H H WILLARD[54] obtains a like result by precipitation from homogeneous solution, a method that is based on the gradual production of reactants by hydrolysis The province of the genetic formation of materials also includes a consideration of the fact that amorphous and in particular gelatinous precipitates often exhibit a resistance to H^+ and OH^- ions, which increases with time This is known as aging It may be assumed that aging, which is connected primarily with modification of surface, will manifest itself in the behaviour of the materials towards still other chemical agencies, and this can be of considerable importance to analytical chemistry It seems that the possibility of new reaction paths is not excluded when dealing with aged precipitates. This has been demonstrated in the case of nickel hydroxide Freshly precipitated nickel hydroxide reacts with potassium periodate to produce nickel periodate, whereas ripened nickel hydroxide gives higher nickel oxides A new test for periodate is based on this unexpected finding[55].

Topochemical reactions which can be put to analytical use occur when one of the reactants is not soluble in water Frequent use is made of this situation in spot test analysis as well as in the off-print process for detecting inhomogeneities in metal and mineral sections The coloured reaction products remain at the site of their formation and the sensitivity of the tests is thereby enormously increased Topochemical reactions provide the basis of the protective layer effect[86] the micro-analytical importance being illustrated by the following spot reaction if a drop of a palladous chloride solution is placed on paper impregnated with nickel dimethylglyoxime and the red paper is plunged into dilute mineral acid, the colour is discharged except at the spot fleck Acid-resistant palladium-dimethylglyoxime is formed at the spot where the drop was applied and protects the underlying nickel-dimethylglyoxime from the solvent action of the acid As little as 0 05γ palladium can be specifically detected in this way

The consideration of topochemical reactions poses the question as to the mechanism by which solids react The classic concept that solids react with dissolved reagents solely *via* the portion of the solid that has gone into solution, which is then constantly resupplied, has handicapped the appreciation of the great importance of the direct reactions of ions and molecules residing on the surface of solids In such cases, the reaction products may form an independent solid phase or they may pass into solution However, reaction products may also remain in the phase association of the solid Obviously this is possible only when the reacting portions of the surface in addition or exchange reactions do not leave their phase association An occurrence of this kind corresponds to the concept of chemical adsorption

New ideas concerning adsorption compounds and colour lakes are obtained[87] when the picture of topochemical surface reactions is carried over to solids which are in the hydrosol or hydrogel form The precipitation of adsorption compounds of tannin with metals, based on pioneer work of W R SCHOELLER[88] and so widely used in analysis, has hitherto been regarded as a flocculation of negatively charged hydrosol particles of the tannin with positively charged hydrosol particles of inorganic hydrolysis products[89] This idea is controverted by the occurrence of tannin precipitations through the action of like charged particles (*e g* tungsten trioxide-tannin precipitate) and also by the fact that many tannin precipitates are highly coloured, although according to colloid chemical experience the mutual flocculation of colourless particles produces no colour change Therefore, it is more likely and also consistent with the polyphenol nature of tannin that metal-tannin precipitates are products of topochemical reactions, which take place on the surface of metal hydrosol particles with truly dissolved tannin, as well as of reactions of metal ions on the surface of colloidal tannin particles Analogous topochemical reactions are probably to be assumed in general for the precipitation of adsorption compounds, which are usually characterized by the fact that one of the reacting materials is in the colloidal range[90]

Because of their colour and varying composition, many tannin precipitates are closely related to the so-called colour lakes, the production of which is not only the basis of numerous sensitive and selective tests for metals (including also colorimetric determinations) but also of importance for the technical processes of textile dyeing In the literature, colour lakes are almost always considered as inner complex salts of metals with acid dyestuffs, even though such salts, if they have been isolated at all, have ordinarily been obtained under conditions which do not correspond to those prevailing when the products are formed in analytical or technical processes The weakness of this undue generalization is proved by the aluminium-alizarin lake, which is a model instance of lake formation This material exhibits chemical properties and also has a different colour than the inner complex aluminium alizarinate, isolated in 1913 by A MOHLAU[91] This discrepancy, which hitherto has been completely overlooked, is of interest to the chemistry of s s s reactions where the colour lakes of the type just mentioned are regarded as products of surface reactions of metal hydroxides with dyestuffs, with constitutions enabling them to enter into inner complex binding, the reaction products remaining in the phase association of the solid This viewpoint, which stipulates the same topochemical formation mechanism for colour lakes and tannin-adsorption compounds, does not exclude the formation, under suitable circumstances, of reaction products which closely approach formula-pure inner complex salts[92] Furthermore it can be expected that colour lakes may be formed not only through inner complex binding of dyes on a reactive surface, but also by addition only This was recently demonstrated[93] in the case of palladium cyanide, which retains basic dyestuffs with typical change in colour With basic indicator dyestuffs, the lake colour is essentially identical with the colour of the indicator in the acidic *p*H range (This finding gives an interesting insight into the resonance forms of indicators) The palladium cyanide lakes, whose easy production may serve for the identification of this salt, provide the first instances of metallo-organic adsorption compounds, the inorganic component of which is not a basic or acidic metal hydroxide

Adsorption compounds and lakes show that it is possible through surface reactions to stabilize chemical linkings which cannot be realized in the form of Dalton compounds This opens interesting prospects For example, it gives a plausible point of attack for such problems as reaction anomalies, co- and post-precipitation[44], the masking of components of mixed precipitates *etc* The idea of topochemical surface reactions[45] may also be used when considering the collector action of precipitates This term denotes the retention of traces of co-solutes by certain precipitates during their formation and in many instances after they have aged Since this retention is often selective in character, it has become the basis of important procedures of trace analysis, which is a modern and very useful branch of micro-analysis[46]

Acknowledgement is due to Dr R E Oesper of the University of Cincinnati for translating this paper from the German

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Baking Industries Research Station

Measuring the Physical Characteristics of Bread

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ONE of the major difficulties in bakery research is to assess the characteristics of quality in baked products by scientific methods It is desirable to have in addition to organoleptic tests other methods of assessment removed from the difficulties surrounding the correlation of individual judgements For this reason physical instruments find a place in any complete scheme of quality testing

When bread is scored for quality, many different points are commonly taken into account by the judge Of these only a few are capable of measurement on some instrument However, the reliability of these instrumental readings compensates to some extent for their limited scope and enables them to be put to a variety of uses in the laboratory or in the bakery Their chief asset is their sensitivity Much smaller changes can be detected than by subjective assessment, which finds immediate use in production control For research purposes the effect of changing ingredients or processing can be detected and measured and the relative importance of such variables determined

In developing suitable test procedures the aim is to provide sufficient sensitivity in the simplest manner possible A limit to the sensitivity required in any application is set by the variability between loaves within a batch, and when this is the factor which limits the accuracy the sensitivity of the test is sufficient for practical purposes

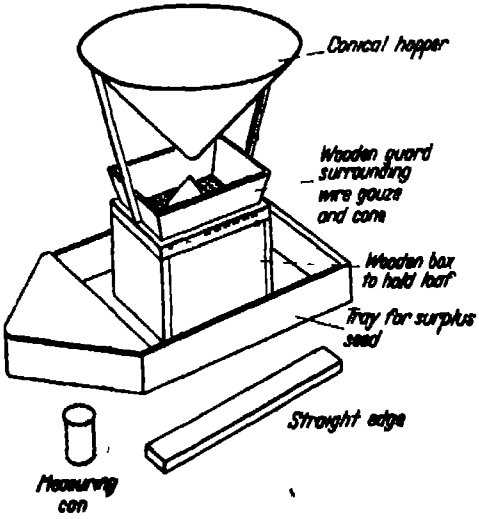

Figure 1. The loaf volume apparatus as constructed for measuring 14 oz tinned loaves

Four different types of instrument have been developed for measuring loaf volume, crumb firmness, toughness and gumminess These properties do not by themselves give a fair estimation of bread quality, there are many other aspects The instruments are, however, of great service, largely on account of their sensitivity and their objective nature

THE LOAF VOLUME APPARATUS

This apparatus was developed to meet the need for an accurate measurement by simple and reliable means Many other types have been described previously, the present apparatus being developed from a simple type introduced in 1938 by W H CATHCART and L C COLE[1] by a slight elaboration which has the effect of reducing the error of the original form to less than half

The apparatus, which is shown in *Figure 1*, consists of a rectangular wooden box of dimensions convenient to contain the loaf with space all round and a special pouring device which fits over the top of the box This is for the introduction of seed into the box to fill the space around a loaf contained in it in such a way as to secure even packing of the seed The packing error is the chief difficulty to be overcome in measuring loaf volume and all types of apparatus are designed with the object of overcoming it The seed used is pearl barley Rape seed has been widely recommended, but when tried in the apparatus was found to give no improvement Pearl barley has the advantages of being cheap, easily obtainable and convenient to handle During manufacture it is dried to a low moisture content and keeps well.

The pouring device consists of a large conical hopper to hold the 7 lb (3 2 kg) of barley used and having a ⅝ in (16 mm) diam hole at the bottom to regulate the flow The seed impinges on a cone which is fixed on the centre of a piece of $\frac{5}{16}$ in (8 mm) wire gauze The cone deflects the seed to the side of the box, while the gauze scatters it and produces a uniform speed. The seed is prevented from overflowing by a wooden guard.

In use, the apparatus is placed in a large tray, the bottom of the measuring box is covered with a fixed amount of seed, the loaf is inserted and the pouring device fixed above the box. All the seed is inserted into the hopper and allowed to run through. The pouring device is then removed and the seed levelled to the top of the box by drawing a wooden straight-edge across it, the edge being tilted slightly forwards. The box is not tapped. The surplus seed is then removed from the tray, the seed is emptied out of the box and weighed. The weight of the seed required to fill the space around the loaf is a measure of its volume and the apparatus can be calibrated to give a direct conversion.

The apparatus is calibrated using wax coated loaves, as recommended by J G MALLOCH and W H COOK[2]. A series of loaves of different volumes is coated with paraffin wax to make them waterproof and the volume can then be determined by direct displacement of water in a *Eureka* can. It is essential to use loaf shaped objects for the calibration as the seed will pack differently around objects of different shape. This is prevented from causing error for different shaped loaves by the cone above the wire gauze, but the use of, for example, rectangular blocks for calibration would not be permissible.

To check the reproducibility of the results, a series of ten readings was taken with the apparatus on each of six loaves used for calibration. The coefficient of variation was found to be 0·20 per cent. To show that this accuracy is adequate, a series of twenty similar loaves baked on the same day and hand-moulded by the same baker is measured. The coefficient of variation was 2·9 per cent. A satisfactory degree of accuracy is thus attained. The apparatus is in fact believed to be more accurate than any other type. If it is required to test other sizes or shapes of loaf an apparatus for the purpose is easily constructed and can be designed to use the minimum quantity of seed, an important design consideration to achieve maximum accuracy.

CRUMB FIRMNESS

For representing crumb firmness by a single figure, a simple compressimeter has been designed and a standard procedure based on the measured characteristics of bread crumb is applied. The compressimeter, which is shown in *Figure 2*, contains two brass plates, between which the crumb sample is compressed, the lower plate being fixed and the upper plate constrained to move up or down vertically. To the upper plate is fixed a platform on which weights may be applied and to this is attached a string passing over a pulley to a counterweight. The movement of the pulley is indicated by a pointer attached to its spindle, which latter runs in ball bearings. In use, a circular sample 3·2 cm diam is cut from the centre line of a slice of bread 1 cm thick taken from as near the centre of the loaf as practicable and 2 cm from the bottom crust, using a sharpened pastry cutter.

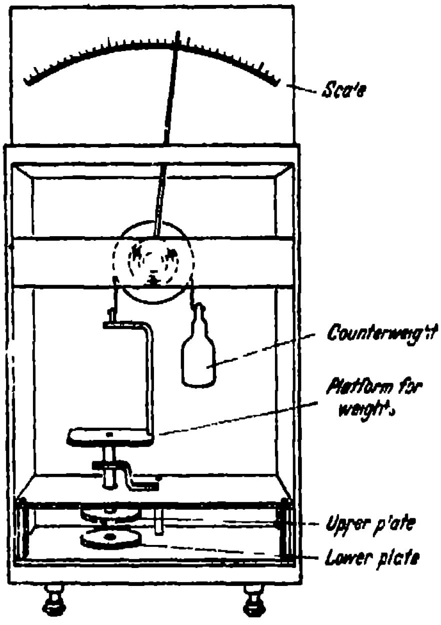

Figure 2 The compressimeter for measuring crumb firmness

Before a satisfactory test procedure was evolved, a good deal of experimental work was carried out. It was found that when a weight is applied to the platform above the test sample, the compression increases fairly slowly to a more or less constant value, taking about 1 minute or so to steady. After one minute, the reading is substantially constant for practical purposes, although it continues to increase slowly and linearly for a considerable time, the initial increase being exponential. If then the weight is removed the sample slowly recovers practically all its deformation, with the provisos that the atmosphere is sufficiently moist to prevent appreciable drying of the sample, which prevents complete recovery, and the weight used has not been so large as to completely flatten the sample. It is impossible to prevent drying entirely as the equilibrium humidity of bread crumb is over 90 per cent. Now, if the test is repeated on the same sample, the same readings are again obtained, if the sample has been allowed about 10 minutes to recover. By using different weights each time and leaving each for the same time, a number of readings of weight versus compression can be obtained, from which a stress/strain curve can be plotted. This curve, of which a typical example is shown in *Figure 3*, is of peculiar shape. The initial portion, for small stresses, is parabolic. Then, as the weight increases the curve bends over and a sudden large increase in strain occurs for only a small increase in stress until, as the cells collapse,

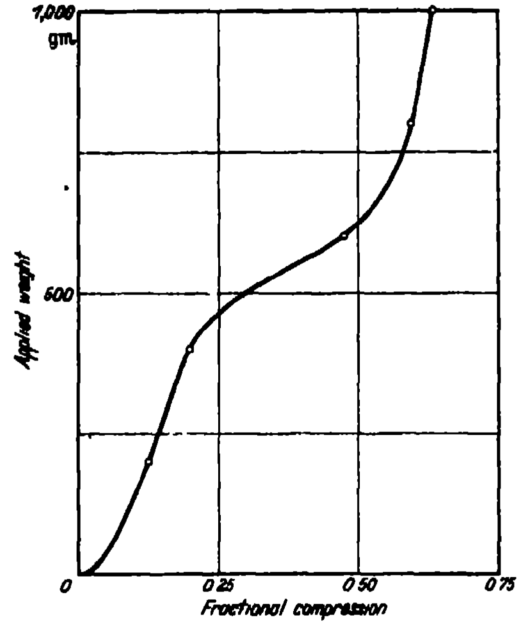

Figure 3 A typical stress/strain curve for bread crumb

the resistance again increases. This curve is similar in some respects to those published by L B CROSSLAND and H H FAVOR[3]. It is found that all stress/strain curves exhibit similar characteristics, having a point of inflection at a strain (compression/original thickness) of about 0.3 to 0.4. Stress/strain curves were then obtained for samples of different areas and different thicknesses. It was found that the stress required to produce a given strain is proportional to area of cross section, but the compression produced by a given force was only proportional to thickness for strains of 0.5 or larger. For small strains of 0.1 or so the compression was almost constant for different thicknesses.

This is one factor which influenced the choice of a routine test. The other important factor is the reproducibility of the readings. If percentage accuracy is considered, then the best reproducibility is obtained for strains between 0.3 and 0.5. Accordingly the test chosen to give a numerical indication of firmness is to find the weight required to give a strain of 0.5, using a cutter of a particular area of cross section. The results using cutters of other areas can be compared if the readings are divided by the area.

The method of carrying out the test makes use of the experimentally determined fact that if a weight is applied to a test piece for one minute, and then a further increment of 50 gram is added and left on for a further minute, the resulting compression is the same as if the whole weight had been applied for one minute, within the experimental error. This process of incrementing the weight applied at intervals of one minute can be repeated about five times without loss of accuracy. This enables a series of trials to be made under increasing weights until a compression of half the original thickness is obtained. The weight nearest to this is noted as the figure for firmness. Thus, firmness figures are obtained to the nearest 50 gram. The cutter size which has been found most convenient has a diameter of 3.2 cm and an area of 8.02 sq cm.

Although firmness is an important factor, the test is not a very sensitive one as there is a considerable variation between loaves. In a recent test on eighteen similar hand-moulded loaves, using the above procedure, the variance* between loaves was about 8,000 gm^2 while the variance between slices, which includes the experimental error, was 700 gm^2. The average firmness in this case was 506 gm, compared with which the standard deviation of 93 gm is considerable. This defect is minimized in practice by taking the average figure of three loaves. It would seem, however, that a mechanical system of processing is desirable to reduce the variability between different operators and the same operator at different times, as the test is frequently used to detect fairly small differences introduced by changing a single processing or ingredient variable.

The test for firmness may be carried out after various periods of storage, whereby the effect of storage conditions and the relative effect of different processing and ingredient variables on the rate at which firming takes place may be determined.

TOUGHNESS OF BREAD CRUMB

This is measured with the instrument shown in *Figure 4*, known as a tenderometer. It is a simplified version of an apparatus described by G W ROBINSON[4]. A

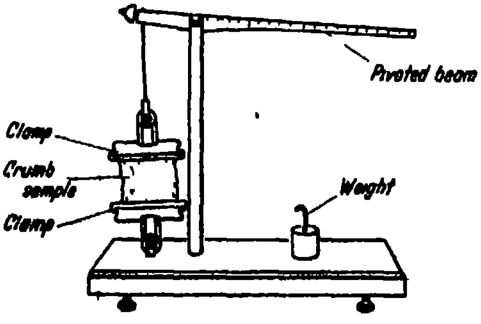

Figure 4 The tenderometer for measuring the toughness of bread crumb

sample of crumb of standard dimensions 7 × 5 × 1 cm is fixed between the two paper clamps which have been adjusted so that they will only partly close and grip the bread firmly without crushing it The lower clamp is fixed, the upper clamp is attached by a string to one side of a pivoted beam On the other side of the beam a weight is hung, which is moved outwards until the bread breaks The force required to break the sample is a measure of its toughness This measurement is not correlated with firmness

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* The sum of the variances due to each factor is equal to the total variance, which equals the square of the standard deviation.

THE TACKMETER

For detecting and measuring gumminess or doughiness in bread crumb, the simple tackmeter illustrated in *Figure 5* is used A whole slice of bread is placed under a brass disk 4 6 cm diam which is pressed into it by a screw clamp to expel the air from it, the top of the disk being attached by gut to one arm of a pivoted beam After leaving for two minutes the clamp is removed A weight is then moved along the other arm of the beam until the disk is pulled away from the bread The force required for this is read from graduations on the beam and is a measure of gumminess Instruments similar in principle are used in other industries *e g* for printing inks, but this type of instrument has not been used previously for bread

In the case of the two latter instruments the accuracy obtainable is more than sufficient for the purpose The toughness varies between samples from the same loaf as well as between loaves and this limits the accuracy with which it is useful to specify the factor for a particular loaf The standard deviation between slices of a loaf was 20 gm for an average value of toughness of 223 gm in a particular experiment It is therefore only useful to specify the toughness figure to the nearest 10 or 20 gm and this is easily obtainable

Similarly, for gumminess a standard deviation of 190 gm between slices with an average figure of 2,660 gm was obtained in a particular experiment It is thus only useful to record the gumminess figure to the nearest 100 or 200 gm and this also is easily arranged

USE OF THE INSTRUMENTS

At present these instruments are being used to find the effect on the resultant bread of altering any single variable, either processing or ingredients Some variables are found to have little effect by themselves, but there are so many variations possible that there may be a cumulative effect if quite small factors are not watched carefully Also, a slight change in the flour quality alters its properties considerably, so that the main ingredient is changing all the time, sometimes very drastically The amount of water taken by the flour, its water absorption, changes with each sample The correct quantity of water is determined by a water absorption meter[8] which aims at bringing the elasticity of a mature dough to a constant value

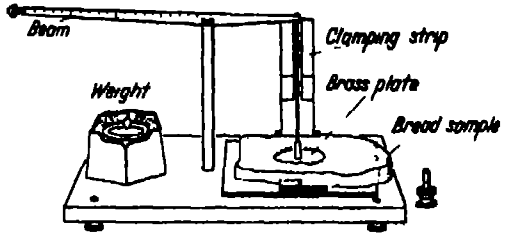

Figure 5 The tackmeter for measuring gumminess

For each test, in order to keep all the factors as constant as possible, a standard baking procedure is used Using the basic formula and procedure, a batch of six fourteen oz (*c* 400 gm) tinned loaves is prepared With a single modification, another batch of six loaves is prepared at the same time These are cooled and stored under constant conditions for approximately 24 hr The batches are then weighed and volume determinations are carried out on four loaves from each batch Three loaves from each batch are then tested for firmness, toughness and gumminess, the remaining three being wrapped in moisture-proof cellophane, and stored at a constant temperature until five days old, when they are tested

It is found that when the loaves are first baked their properties are changing rapidly and the bread is so soft that testing is very difficult After 24 hr, testing is easier and also firmness has settled down to a constant rate of increase which is maintained for many days The changes in the properties, measured after five days, indicate the progress of staling This is an important factor, but one which is not easily assessed In addition to the physical properties measured in these tests, staling is indicated by such factors as mastication, crumbliness, condition of crust *etc* as well as flavour In practice, however, it is found most useful to have an accurate, objective measurement of the increase in firmness It is found that this property can be reduced by the addition of certain ingredients *e g* compound cooking fat, glyceryl monostearate, polyoxyethylene monostearate[6] *etc* and the effect of these and other ingredients have been and are being extensively studied.

To find the effect of each variable on the properties of the resultant bread is the best way of maintaining and improving its quality The relative importance of each variable can be established although its effect will vary somewhat from one flour to another This shows where the most careful control is needed in the processing and enables the effect of improving ingredients to be compared These results translated into simple practical instructions can then be made use of by the baker to improve his product.

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Miscellaneous Notes

RUTHERFORD MEMORIAL FUND

The Council of the Royal Society appeals for financial support for the creation of a suitable memorial to that great figure in twentieth century science, the late Lord Rutherford of Nelson

A special committee set up by the Council of the Royal Society has for some time considered the most suitable memorial, and it is thought desirable that this should take two forms

1 Rutherford Scholarships tenable for three years, to be awarded to post-graduate students within the British Commonwealth, for research in the natural sciences with a preference for experimental physics A scholar will normally be required to carry out his research in an Institution in some part of the British Commonwealth other than that in which he graduated

2 A Rutherford Memorial Lecture to be delivered at intervals at selected university centres in the British Commonwealth overseas, at least one in three to be given in New Zealand

It is proposed also to arrange for the collection, arrangement and binding of copies of Rutherford's correspondence, and its preservation in safe custody for future reference

For these purposes a substantial endowment fund will be needed, and it is hoped that this appeal will meet with a generous response Contributions may be sent to the Rutherford Memorial Committee, The Royal Society, Burlington House, London, W 1, or contributions from the United Kingdom may be made by covenant over seven years

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

Joint Fire Research Organization— The Report for 1949 has recently been published

Some progress has been made in studies of the growth of fire in buildings by means of laboratory experiments with small models A series of large scale experiments was carried out in which the performance of certain types of construction in the standard test furnaces was compared with their behaviour under practical fire conditions in houses Tests in the furnaces were followed by full scale tests in a mock living room complete with rough furniture The time of failure in the actual fire was similar to that of the furnace tests. Further tests were carried out with pre-stressed concrete and with steel beams protected by gypsum products The laboratory study of the hazard of the ignition of structural material by flue-pipes was continued The lower part of a flue may reach a temperature of nearly 1,500°F (*c* 820°C) under certain conditions when a closable stove is in use The temperatures reached on the surface of wooden panels near the flue, with and without a protective covering of asbestos, have been measured and safe distances for use of combustible structural materials determined

An electrical machine was made which will indicate the rise in temperature throughout various types of structure when the face of the specimen is heated according to the standard time/temperature curve The machine enables a considerable saving in time during experimental work

A comparative study of foam compounds was made on fires in petrol and certain industrial solvents, such as industrial methylated spirit The rate of destruction of hydrolysed protein foams on alcohol fires was too rapid to be overcome by a reasonable increase in the rate of delivery Certain types of chemical foam were most satisfactory

INTER-SERVICE METALLURGICAL RESEARCH

Standardization of sizes of tubes made from special refractories— The Sintered Oxides Sub-Committee has held discussions with manufacturers with the aim of improving the supply of tubes of special refractory. Delay in the delivery of these items arises mainly from the large number of different sizes which are demanded by the users, making it difficult for the manufacturers to maintain stocks.

It has now been agreed to concentrate on production of a range of sizes which are to be regarded as standard henceforward The sizes adopted have been chosen after careful consideration of the demand for tubes in recent years, and it is hoped that they will fulfil the requirements of most users The manufacturers have undertaken to maintain stocks of the standard sizes, so that orders may be met from articles in stock The success of this attempt to provide better supplies of tubes will depend of course on the wholehearted cooperation of the users In particular, those employing large numbers of tubes are asked to standardize their sizes at the earliest possible moment and those designing new apparatus are asked to use standard sizes wherever possible Production of the standard items will commence immediately Non-standard tubes will be obtainable, but their delivery may still be subject to delay

Tube standardization details are as follow

1 The materials involved are *a* impervious alumina and *b* impervious mullite for use at temperatures up to 1,700°C The descriptions of the two classes of special refractory are those agreed by the manufacturers, who will provide details of the properties of their products on request

2 The cross sections of the standard sizes are

Int diam (mm)	5	10	15	25	40	50	65	75
Wall thickness (mm)	1 5	2 0	2 5	3 0	4 0	4 5	5 0	5 5

All tolerances will be as stated by the individual manufacturers Metric sizes are adopted in view of the present trend in that direction and because many special refractory tubes are used in research, where the metric system is usual

3 All standard tubes will be available in lengths up to 900 mm with both ends open, and also with one end open and the other hemispherically closed

Thermocouple insulator— While dealing with tube standardization the opportunity has been taken to introduce a standard cross section of impervious alumina twin-bore thermocouple insulator It will have oval section, with 3 5 mm major and 2 0 mm minor axes, *1* mm bores, *1* 5 mm between centres

NATIONAL RESEARCH COUNCIL OF CANADA

Applied Chemistry Branch— The organic synthesis section now consists of two groups, engaged respectively on i chemistry of ethylene oxide, and ii preparation of organic compounds containing stable or radioactive isotopes

Interest in the first subject arose from the considerable amount of work done on the catalytic oxidation of ethylene Reactions of ethylene oxide with water, halogens, and amines are being studied The main object is to determine the mechanism of these reactions and their reaction rate constants An improved analytical method for the quantitative estimation of ethylene oxide has been developed. The programme is being extended to include a study of the organic cyclic oxides

In some instances of the work done by the second group, new methods of synthesis have been developed to obtain the labelled compounds required Some of these special chemicals have been used in nutrition experiments at the Dominion Experimental Farm, others, such as a series of deuterium-labelled compounds, for spectroscopic and other studies by NRC or university research teams

CORRECTION

Page 507, line 24, R H column should read
'is not a naphthodioxane but bi-1,3-dioxa*cyclo*-pentyl(2)'

New Books

Introductory Statistics

M H QUENOUILLE

(*xii+248 pp, 10 in by 6 in*)

London Butterworth-Springer Ltd 30*s*

Dr Quenouille's book places him in the small class of those who have something new to say about familiar problems. Even his numerical examples have a refreshing quality most of the data are used for the first time, as illustrations of statistical technique, very few examples are merely statistical exercises that have no practical application, and the Poisson distribution is illustrated without the aid of Prussian cavalry

The nine chapters describe, concisely but clearly, the most important methods of statistical science, primarily with reference to biometry but also with mention of applications in the social sciences Most of each chapter is concerned with elementary applications of statistical techniques, but supplementary sections show some of the theory and more advanced ideas A good introduction to analysis of variance and experimental design is given, though the reader will need further study before he is fully equipped for planning his own experiments The chapter on covariance analysis is particularly valuable, in that it describes clearly methods often thought too difficult for an elementary text Best of all, perhaps because it is concerned with an aspect of the subject in which Dr Quenouille is himself making notable advances, is the chapter on transformations Most writers and teachers slur over the logical and mathematical problems involved in the analysis of transformed data , this book provides the basis for a comprehensive discussion from which future students will benefit

D J FINNEY

Vision and the Eye

M H PIRENNE

(*xx+187 pp, 109 illus, 7¼ in by 5¼ in*)

London Chapman and Hall Ltd, 1949 12s 6*d*

A NUMBER of books on vision has appeared recently and each has had its own special contribution to make to the subject Dr PIRENNE has been especially associated with work on visual thresholds and particularly with the effect which the quantum nature of light might have on measurements of visual sensitivity by the threshold technique, and although this interest is reflected by three chapters devoted to the topic, the book as a whole provides a more general survey of visual physiology

The opening chapters deal with the structure of the eye and the retina, followed by chapters on the spectral sensitivity of the retinal receptors and on electrophysiology We then have the group of chapters on thresholds, another group on visual acuity, another on colour vision, with final chapters on binocular vision and on what might be termed the visual philosophy of the author Among the numerous illustrations, those of the retinal mosaic, the retinal structure of animals and birds, and of the eyes of insects are especially instructive

The subject of vision has become rather notorious for its acrimonious discussions, but these have very often had their origin in misunderstandings associated with the subjective nature of many visual experiments Pirenne has deliberately tried to avoid this treacherous ground, basing as much of his information as possible on objective physiological data—histology, electrophysiology and the like There is a great deal to commend this approach, so that when subjective phenomena do have to be interpreted, the physiological possibilities can be explored before relegating the effect to the psychological hinterland

At the same time we have to recognize that the mind and consciousness are an integral part of the visual process and Pirenne's final chapter is an acknowledgement of that fact Some readers may well feel that this chapter should mark the starting point for a book on vision rather than its end Each one to his own choice, but for those who wish to study the eye in the first place as a light-sensitive instrument, this book will prove a most interesting introduction

W D WRIGHT

Ionization Chambers and Counters
Experimental Techniques

B B ROSSI and H H STAUB

(*xviii+243 pp, illus, 9 in by 6 in*)

New York and London McGraw-Hill Book Co , Inc ,
1949 $2 25 or 19s 6*d* net

Counting Tubes . Theory and Applications

S C CURRAN and J D CRAGGS

(*xi+238 pp, 119 illus, 9¾ in by 6 in*)

London Butterworths Scientific Publications, 1949 35s
New York Academic Press Inc , 1949

TWO books have appeared dealing with the measurement of radioactive radiations Unfortunately they were written just prior to the extensive development of scintillation counters for particle and high efficiency γ-ray counting and prior to the recent use of proportional counters by CURRAN and others for precise energy measurements of low energy x-rays and electrons In consequence these important developments are dealt with only very briefly and the contents of the books concern mainly the use of Geiger-Müller counters and ionization chambers

The first book is one of the volumes in the United States National Nuclear Energy Series and is published under the auspices of the Atomic Energy Commission Both its authors were leading scientists at the Los Alamos Laboratory during the war and the book may therefore be considered as an account of technical practice at the end of the war in the use of ionization chambers and counters The first four chapters of the book deal with basic physical principles After an introduction describing the behaviour of electrons and ions in gases, a description is given of the theoretical and experimental basis of ionization chamber operation first for a continuous source of ionization and secondly for individual events such as charged particle tracks where ion collection times have become a most important factor A further chapter discusses the multiplication process in gases

Of the remaining chapters of the book, one is devoted to Geiger-Müller counters, and ionization chambers for β-, γ- and x-ray detection Three chapters are devoted to ionization chambers for the detection of α-particles, neutron recoils, and slow neutrons A final chapter gives much useful information on fission detectors Experimentally determined range/energy and absorption data are collected together in an appendix

Counting Tubes is a book preoccupied mainly with the Geiger-Muller counter on which subject both its authors write with considerable authority The book contains introductory chapters on the elementary theory of ionization chambers and counters, the kinetic theory of the ionization processes in a gas and the subject of proportional counting Chapters follow on the Geiger-Müller counter with simple gas filling and with a quench gas filling A discussion is given of the efficiency of counters for particle detection, counter resolving time and the use of counters in coincidence techniques The electrical circuits associated with Geiger-Muller counters receive detailed treatment The remaining chapters of the book are devoted to a discussion of the uses of these counters for cosmic ray and nuclear physics research and for technical applications of radiations such as radioactive tracer studies Brief reference is made to scintillation, crystal and spark counters

The book by Rossi and Staub is primarily a teaching manual and contains hardly any references Curran and Craggs, on the other hand, have included a most comprehensive bibliography and their book is mainly for the research student who is a counter specialist, though it has much of interest to the general reader

J V Dunworth

The Elements of Genetics

C D DARLINGTON and K MATHER

(*446 pp, 88 illus, 31 tables, 8½ in by 5½ in*)

London George Allen and Unwin Ltd, 1949 25*s* net

The joint authors of this book have made it their task to place genetics at the corner stone of the biological sciences While the conception has great merit, the execution is not a success To their respective fields, of chromosome cytology and the statistical analysis of genetical data, C D Darlington and K Mather have both made extensive and valuable contributions the parts of the book dealing with these two aspects of genetics are handled by craftsmen who thoroughly understand their trades

Where other aspects of genetics are considered and more especially where other sciences are drawn into the picture the treatment is slipshod, unprecise and sometimes incorrect.

The book is frankly speculative, as its authors state in the preface Speculation may be valuable and stimulating it is so only when recognizable as such A major criticism of this book is that the same language is used for statements of proven fact as for speculation The book abounds in *ex cathedra* statements of which two examples may be mentioned for illustration The loss of sight in cave animals is stated to be a correlated response to selection for other characters such as sense of touch This may well be true, but experimental evidence is entirely lacking It is stated that desoxyribose nucleic acid is converted to ribose nucleic acid during the transformation of telophase nuclei to the 'resting' condition Again this may be true, but no biochemist would dare to state it as proven fact

The title of the book might be taken to have one of two meanings It might either be a textbook of genetics aiming to provide the student with an authoritative account of the subject, or it might be a more specialized treatise on the theory of the gene in biology comparable in importance and position to the atomic theory in physics It must be stated regretfully that this book falls far short of fulfilling either function

H G Callan

Electron Microscopy Technique and Applications

R W G WYCKOFF

(*x + 248 pp, 202 illus, 9 in by 6 in*)

New York Interscience Publishers, Inc, 1949 $5 00
London Interscience Publishers, Ltd, 1949 40*s*

In the two decades since it was invented several books about the electron microscope have appeared, dealing principally with its underlying principles and the technical details of its construction Dr Wyckoff has now written the first book that begins to do justice to its applications He sets out to describe the uses to which the instrument may be put in his own field of work, which covers a large part of the no-man's-land that is beginning to be recognized as biophysics Having been one of the first scientists in America to use it as a research tool, and having had many years of prior experience in applying other physical methods to biological problems, he is one of the two or three best qualified to assess its achievements Although the illustrations are drawn entirely from his own laboratory, he surveys generally the work done in each of his particular spheres of interest, and succeeds admirably in his aim Anyone who wishes to understand what light the electron microscope can throw on the morphology of bacteria and viruses, the macromolecular structure of fibrous tissues, or on the nature of macromolecules themselves, will find here as concise an account as could be desired

The work must be judged for what it sets out to be, from a wider standpoint it has the deficiencies which are the inevitable counterpart of the merits of a personal document Writing directly out of his own experience, the author has complete mastery of his material and achieves a clarity and simplicity of style which might well serve as a model of scientific exposition. At the same time it is natural that he should have developed principally those techniques of microscopy which were most useful in his immediate problems of research, to the neglect of others For instance, the detailed procedures for shadowing specimens with heavy metals, in order to increase the contrast in their image, are very fully described —as would be expected, since Dr Wyckoff was chiefly responsible for introducing them into electron and optical microscopy But there is no discussion of the limitations of the shadowing method nor of its possible dangers in uncritical use, nor of the place of unshadowed micrographs Indeed, every micrograph reproduced is of shadowed materials, and the uninitiated will be unable to judge the contrast and resolution obtainable from unshadowed specimens The question is particularly important where routine examinations have to be made and the time spent in shadowing would unduly lengthen the work, whilst perfectly satisfactory results could be obtained with unshadowed surface replicas This is especially true in metallurgical applications, which receive little notice here Similarly the technical hints on operation relate only to the R C A machines, without giving the fundamental principles which would allow them to be applied to any other type of microscope having different control mechanisms In short, the book gives a restricted account of specimen techniques and a number of valuable hints, drawn from hard experience, on the operation of the electron microscope. It is not, and does not pretend to be, a comprehensive manual of the preparative and instrumental techniques of the subject

It will, therefore, be primarily of value to those who already have some acquaintance with one side or another of the subject to the operator who wants to know how to improve his methods of aligning the microscope or of shadow-casting specimens, for example, or to the biologist or medical man who seeks an authoritative estimate of the capabilities and limitations of the new instrument Its value to the latter is greatly enhanced by the numerous plates and by the very full bibliographies of original papers which are classified by subject and appended to each chapter To the non-biologist, the later chapters on the investigation of the formation of fibrous matter from globular molecular units, and of the nature and crystalline form of the plant viruses, will probably be of greatest interest They give a fascinating picture of the advance from the molecular side towards a better understanding of living processes In addition, there are introductory chapters outlining the principles of the electron microscope and the construction of the models commercially available, with some discussion of their relative merits, which will be valuable especially to the non-physicist new to the subject The book, as might be expected, is finely produced as well as excellently written, the reproductions of micrographs being of very high quality They will come as a revelation to many who have not been aware of recent developments in the technique of electron microscopy

V E. COSSLETT

Surface Active Agents Their Chemistry and Technology

A M SCHWARTZ and J W. PERRY

(*xi+579 pp, 50 illus, 9 in by 6 in*)

New York Interscience, 1949 $10 00
London Interscience, 1949 60s

THE book is divided into three parts, the first, consisting of processes for synthesizing and manufacturing surface agents, constitutes approximately half the book, the other two parts are given over equally to the physical chemistry of surface active agents in theory and practice, and the practical applications of surface active agents

In the very nature of things, to give justice to these fields of knowledge in one book is an impossibility But whereas many attempts have been made to produce textbooks for the latter two sections of this book, there is, to the reviewer's knowledge, no comprehensive publication on the organic chemistry of surface active agents available to the world Consequently, the first half will be a very valuable and essential contribution to scientific literature This section, on the processes for synthesizing and manufacturing surface active agents, is excellent; it is difficult to find an agent however obscure which is not mentioned in detail The authors have managed to produce order in a field of science which industry has intentionally kept vague and extremely puzzling by using a variety of baffling trade names The many different compounds made for certain purposes have usually proved very valuable in fields quite different from those for which they were originally intended. It has been difficult to find out from the trade name, the chemistry of the main compound and that of the additives, together with their relative proportions. This has now been made much easier and clearer by this section of the book

Besides sections on the more standard surface agents, there are interesting chapters on little known commodities such as non-ionic and ampholytic surface active agents, organic and inorganic builders and mixtures *etc* The patent reference literature is very comprehensive

The rest of the book would be useful to a student requiring a general knowledge of the physical chemistry and applied fields of surface active agents, but would not be very useful to a specialist For him indeed the first half of this book, with perhaps a section on 'Relationship of surface activity to chemical constitution', would be really indispensable

J H SCHULMAN

Two Lectures

I Present Situation in the Theory of Elementary Particles

II Electron Theory of Superconductivity

W HEISENBERG

(52 pp, 9 illus, 7½ in by 5 in)

Cambridge University Press, 1949 3*s* 6*d* net

THESE two lectures, which were delivered at the Cavendish Laboratory in December 1947, deal with two fundamental problems in theoretical physics In the first the theory of elementary particles is discussed The divergencies which arise in ordinary relativistic quantum theory at the closest distances between interacting particles are, in HEISENBERG's view, not unexpected (§1) since a satisfactory theory of elementary particles must contain as fundamental constants not only h and c but also a length l ($\sim 10^{-13}$ cm), as the mass of a particle cannot be derived from h and c alone (§2a) During the course of the lecture the idea of a primary Hamiltonian which takes into account all elementary particles simultaneously is developed (§§ 2b, 2c, 3a and 3b) and finally rejected (§§ 3c and 3d) in favour of the S-matrix method The only obvious analogy with BORN's more recent approach is that all particles are to be treated by a uniform method. As regards the rest masses of the elementary particles nothing as definite as BORN and RODRIGUEZ's results has been obtained and there is nothing in Heisenberg's approach which might correspond to Born's principle of reciprocity.

In the second lecture, Heisenberg bases his discussion on a condensation phenomenon which, he believes, occurs in a thin layer at the surface of the Fermi sphere in virtue of the Coulomb interactions between the electrons. Since the electrons have the same velocities but different directions at the Fermi surface, the electrons near this surface can form spontaneously closed current circuits The currents can be ordered by an electric or magnetic field and a total current results In these ideas, and the explanation of the Meissner effect, Heisenberg follows the previous work of KRONIG, SOMMERFELD and BETHE, and of F and H LONDON A magnetic field is considered to produce currents only through the Meissner effect and destroys superconductivity in this way Some assumptions of the theory can be criticized, and its basis differs entirely from the theory of BORN and CHENG which is based on a correlation between superconductivity and lattice structure

This book should obviously be read by all specialists, but it will be of great interest also to those non-specialists who desire to follow for themselves the hard but exciting process of searching for new theories and greater understanding

P T LANDSBERG

Die Technischen Grundlagen der kinematischen Zellforschung

Vorschlage fur eine exakte wissenschaftliche Mikrokinematographie

W KUHL

(viii+185 pp, 57 illus, 9¾ in by 6½ in)

Berlin Springer-Verlag, 1949 *DM* 26 00

THE subject of this book is the use of the cinema camera to record the change and movement of living cells and organisms In this branch of biological research Professor KUHL is a distinguished figure. At Frankfurt am Main for the past fifteen years he has used cinematophotography for this purpose in the Institute which he founded and has since directed His studies are mainly embryological, and include investigations on the development of the sea-urchin, and other marine invertebrates, and on the cleavage of Amphibian and Mammalian ova

The apparatus and techniques which Professor Kuhl uses are described, as also are the methods which he has developed for analysing his film material, which the author rightly regards of great importance For Professor Kuhl, it is not enough to produce an elegant film of a living process, the real purpose of such records of biological events is to serve as research material from which quantitative data can be extracted Thus he has used his films to measure the velocity of wandering cells, and the rate of formation of the fertilization membrane of the sea-urchin egg.

Professor Kuhl restricts his description to the techniques which he himself uses at Frankfurt. It appears that the 35 mm gauge of film is used exclusively, the apparatus is elaborate and must have been extremely costly A biologist, on reading this book and contemplating the use of cinema techniques, might well be discouraged by the formidable nature of the machinery involved He might thus overlook the fact that adequate results can be obtained on sub-standard film with much simpler apparatus It is even true to say that the 16 mm gauge has certain advantages exclusive of economic considerations

The value of this book would have been greater if Professor Kuhl had not concentrated so largely on technique but had given space to illustrate more of his results His work is not well known outside Germany, and as far as the reviewer is aware his films have never been shown in this country The various hindrances to the international distribution of scientific films are not yet surmounted and it is highly desirable that such films as those of Professor Kuhl should become accessible

Meanwhile, it would be greatly appreciated if Professor Kuhl could favour us with a further review on the general subject of the results which he has obtained

A Hughes

Excited States of Nuclei

S DEVONS

(x+158 pp, 27 illus 8½ in by 5½ in)

Cambridge University Press, 1949 12s 6*d* net

Dr Devons has written a very competent and interesting monograph about the excited states of nuclei For this reason he deserves the gratitude of all those who work in the field of nuclear disintegrations

For most experimental physicists, theoretical papers present, in their usual formalism, a considerable potential wall to be overcome only by a very concentrated effort on the part of the readers One is therefore impressed when a practical physicist writing a book reveals such an extensive digestion of most of the theoretical papers in this field It is in this close connection of theoretical interpretation of the experimental observations that the chief merit of this monograph is found

The book opens with an introduction dealing with the stationary states as the eigenvalues belonging to a Hamiltonian operator operating on functions subject to the boundary conditions required by the physical problems, taking into account degeneracy and the fact that they are pseudo-stationary All this is done in a lucid descriptive way This is followed by an account of the excited states below the dissociation limit of the lowest bound particle It comprises such items as excitation of these states by protons, neutrons, α-particles, deuterons, and the information obtained from the study of the α and β activity of radio-isotopes The experimental methods are described briefly and the results in specific cases related to theory

Chapter 3 deals with the excited virtual states, paying particular attention to the resonance processes Here will be found much of the work on thermal and epi-thermal neutrons, such as mechanical and electrical velocity selectors, time-of-flight methods and crystal spectrometers for neutrons This is followed by a discussion of the resonance effects of fast particle disintegrations

The optical transitions between states form the contents of Chapter 4 The determination of the emitted quantum energy and the measurement of intensity are discussed in detail The clear statements as to how one obtains information about the type of transition (magnetic and electric multipolarity) are particularly valuable

The last chapter entitled 'Nuclear Spectra and their Interpretation' sets out the various models used which one has to consider in view of the insolubility of the many-body problems of mechanics

On the whole the book seems remarkably complete However, one wonders why the S^1 state of deuterium has been left out of the discussion Since the deuteron plays, in some respects, a similar role in nuclear physics to that of the hydrogen atom in atomic physics, it would seem natural to deal with the large scattering cross section of thermal neutrons by hydrogen and refer to its explanation

It is an arguable question, whether one should expect to find a simple derivation of the Breit-Wigner relation in such a book as this After all, one discusses the techniques to obtain certain experimental data, should one not, therefore, be shown the path which leads to one of the most important formulae in the field under consideration However, as the reviewer is not acquainted with a simple and satisfactorily transparent derivation of the Breit-Wigner formula he does not wish to throw stones

In some respects the title is misleading as one anticipates, in a book on excited states, a collection of charts and nuclear levels such as one finds in similar works on the electronic state of the atom. Fortunately, this side of the field has been admirably covered by the articles from members of Professor Lauritsen's laboratory at the California Institute of Technology in Pasadena and published in the *Review of Modern Physics* Both accounts supplement each other and should be read side by side

E. Bretscher

RESEARCH SUPPLEMENT

A Study of Slow Self-propagating Reactions in Solids

R. A W HILL, B Sc, M A, L E SUTTON, M A, D Phil, F R S, R B TEMPLE, B A, B Sc
and (in part) A WHITE, B A

The self-propagation of slow reactions in mixtures of oxidizing and reducing agents has been studied by recording the temperature changes as the reaction front passes a point The results have been used 1 to investigate the stoichiometry of the reactions 2 to test the Mallard-Le Chatelier theory of propagation by thermal conduction 3 to obtain rates and activation energies for the burning reaction This theory appears to be essentially correct, though somewhat inadequate in its simple form

THIS paper concerns work carried out for the Ministry of Supply with the object of gaining more insight into the factors which determine the linear rate of propagation of the reaction front in a compressed mixture of an oxidizing agent and a reducing agent, and into the fundamental processes of such reactions

Previous work on the effects of the more obvious variables showed that the rate is *a* a function of composition, usually exhibiting a maximum *b* proportional to the initial temperature *c* dependent upon the pelleting pressure, the mass of material reacting per second being constant *d* inversely proportional to particle size, being roughly proportional to the area of contact *e* increased by increase of thermal conductivity of the mass

SPICE and STAVELEY[1] have reported work on the very slow reactions which proceed at temperatures just below the ignition temperature in iron/barium peroxide and in iron/potassium dichromate pellets, and also on the relationship between heat evolution and rate of propagation They concluded that

i the pre-ignition reactions involve the non-gaseous diffusion of the oxidizing agent, as atoms or ions

ii for the former system the pre-ignition and the burning reactions are probably quite different, though for the latter they may be more alike

iii the maximum in rate of propagation usually occurs at a higher weight percentage of reducing agent than that for the maximum heat evolution per gram, sometimes at the same one but never at a lower one They attributed this to the stifling of the reaction by the film of product formed on the particles of reducing agent

iv in some systems the combustion reaction is essentially the same over the whole range of composition while in others there is a series of different reactions

A further conclusion can be drawn by placing the oxidizing agents in order *1* of maximum rate of propagation *2* of maximum heat evolution with a given reducing agent, *3* of decomposition temperature There proves to be a better correlation between maximum rate and decomposition temperature than between maximum rate and maximum heat evolution

MALLARD and LE CHATELIER[2] treated the movement of flames in gaseous mixtures on the assumption that the reaction is propagated purely by the forward conduction of heat Such a theory could explain qualitatively the features mentioned above for the rate of propagation of reaction in solid mixtures In this paper it has been tested quantitatively, using an experimental method which is new in this context *viz* the recording of temperature changes as the reaction zone passes a point

To derive an expression for the rate of propagation (*cf* LEWIS and VON ELBE[3]) it is necessary to integrate an equation which expresses the balance, in a thin section, of heat generated by reaction, heat gain or loss by conduction, and heat loss by material movement relative to the reaction zone (see *Figure 1*)

$$Vqd\frac{de}{dx} + k\frac{d^2T}{dx^2} - Vdc\frac{dT}{dx} = 0 \qquad (1)$$

where V is the rate of propagation, x the linear coordinate, q the heat of reaction per gram, d the density of the unburnt material, e the fraction reacted of the component not in excess, k the thermal conductivity, T the temperature, and c the specific heat

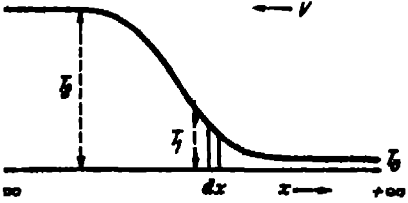

Figure 1

of the unburnt material Putting in obvious boundary conditions, we get

$$Vqd\epsilon + k\frac{\mathrm{d}T}{\mathrm{d}x} - Vdc(T - T_0) = 0 \qquad (2)$$

T_0 being the initial temperature This equation can be solved only if one of the following particular assumptions are made—that T is a known function of x, that ϵ is a known function of x, or that $\mathrm{d}\epsilon/\mathrm{d}t$ (t being time) is a known function of ϵ and T The last procedure has been followed by BELL[4], assuming zero or first order reaction kinetics, and by BOYS and CORNER[5] assuming first or second order kinetics For first order reactions (setting $\mathrm{d}\epsilon/\mathrm{d}t = B(1 - \epsilon)\exp - A/RT$) it can be proved that

$$V^2 = \left\{\frac{kB}{cd}\exp\left(-A/RT_2\right)\right\} \Big/ \left\{\frac{A(T_2 - T_0)}{RT_2^2} - 1\right\} \qquad (3)$$

where T_2 is the final temperature, A is the activation energy, and B is another parameter Earlier, less general treatments are based on the assumption that there is an ignition temperature T_1 below which $\mathrm{d}\epsilon/\mathrm{d}t$ and ϵ are negligible, when equation 2 gives

$$V = \frac{k}{dc}\left(\frac{1}{T' - T_0}\right)\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{T'} \qquad (3a)$$

wherein T' is any temperature below T_1 Also, since $V = \mathrm{d}x/\mathrm{d}t$

$$V^2 = \frac{k}{dc}\left(\frac{1}{T' - T_0}\right)\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{T'} \qquad (3b)$$

Mallard and Le Chatelier made the further assumption that

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{(T_2 - T_1)}{\Delta x} \qquad (4)$$

where T_2 is the maximum temperature and Δx is the width of the reaction zone, when equations 3a and 3b become

$$V = \frac{k}{dc}\left(\frac{T_2 - T_1}{T_1 - T_0}\right)\frac{1}{\Delta x} \qquad (5a)$$

$$\text{and } V^2 = \frac{k}{dc}\left(\frac{T_2 - T_1}{T_1 - T_0}\right)\frac{1}{\Delta t} \qquad (5b)$$

where Δt is the mean reaction time, or ' time width ' of the reaction zone

These expressions show that V is a function of T_2, of thermal conductivity k, and of some parameters expressing reactivity (B and A, or T_1 and Δx or Δt) T_2 in turn is related to the heat of reaction q and the specific heat c Hence, if T_2, k, T_1 and Δx or Δt could be determined the validity of this theory for solid mixtures could be roughly tested through equations 5a or 5b , while if $\mathrm{d}T/\mathrm{d}x$ or $\mathrm{d}T/\mathrm{d}t$ could be measured, it could be tested through the more precise equations 3a and 3b.

If a record of T as a function of t can be obtained it is obvious that values of T_2 and of $\mathrm{d}T/\mathrm{d}t$ would be available , and the other quantities could be measured independently

From such a record it is also possible to obtain a measure of reaction rate which is more precise than the quantity $1/\Delta t$ of equation 5b From equation 1 it follows that if the T/x curve is sigmoid and has a point of inflection ($\mathrm{d}^2T/\mathrm{d}x^2 = 0$) at $T_{i/x}$, then

$$q\left(\frac{\mathrm{d}\epsilon}{\mathrm{d}x}\right)_{T_{i/x}} = c\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{T_{i/x}}$$

whence

$$\left(\frac{\mathrm{d}\epsilon}{\mathrm{d}t}\right)_{T_{i/x}} = \frac{c}{q}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{T_{i/x}} = \frac{1}{T_2 - T_0}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{T_{i/x}} \qquad (6)$$

if c is independent of temperature

Temperature/time records have a further use, since they give values for final temperatures , for from the variation of these with composition some elucidation of the chemical nature of the burning reaction may be possible

EXPERIMENTAL

Systems investigated—These were chosen from those examined by the research group as a whole (see SPICE and STAVELEY[1]) They were iron/barium peroxide, iron/potassium dichromate, sulphur/barium peroxide, iron/potassium permanganate, molybdenum/barium peroxide and molybdenum/potassium permanganate, of which the last three were less completely investigated than the others No binder was employed in pelleting Choice was restricted by such difficulties as the very high temperature and chemical reactivity of some of the slags

From these mixtures the major products are non-gaseous, but some flame commonly accompanies the reaction

The sulphur/barium peroxide mixture was found to undergo two distinct self-propagating reactions—one a slow, low temperature reaction, the other a fast, high temperature one—which, over a certain range of composition, could be separately initiated and investigated

Thermal recording—Temperature was measured with a platinum/platinum-13% rhodium (40 SWG) thermocouple embedded in a pellet of ¼ in diam A special mould was used, with opposite longitudinal slots wide enough to take the couple wires but narrow enough to contain the loose composition , so that after compression the pellet, with couple embedded, could be extruded as a unit The couple was protected by being covered with calcium fluoride, applied by dipping it into an aqueous suspension of the powder, drying, and then heating to dull redness in a flame

The thermal EMF was amplified and applied to a cathode ray tube, the spot being photographed by a drum camera Timing marks were made on the record itself by injecting sharp EMF pulses at appropriate intervals On each record a calibration mark was made by injecting into the amplifier a known EMF, roughly two thirds of the maximum expected, immediately before each run

Temperatures up to about 1,570°C could be recorded

Precision and reproducibility— The results show a considerable scatter, due largely it is thought to the difficulty of preparing identical and uniform pellets despite the facts that one sample of each substance was used for each series of measurements and the pellets were compressed from both ends During burning, moreover, cracking can occur unpredictably and irreproducibly, probably because expansion of the material sets up shearing strains, and this causes irregularity

The values reported for V, T_2, and t are arithmetical means of between two and nine results, usually of three or four Slopes $\mathrm{d}T/\mathrm{d}t$ were obtained from average graphs made as follows All the records for a given composition were first made to coincide at the point, designated zero time, at which they had separately reached one half of the final EMF Arithmetical means of the EMF's at convenient positive and negative times were then evaluated and plotted to give mean temperature/time curves from which, knowing V, mean temperature/distance curves could also be derived

Typical figures are quoted in *Tables I* and *II* to illustrate the reliability of the quoted results *Table II* indicates the general reproducibility of the temperature records The figures are ordinates proportional to the thermo-EMF's at the times indicated and are roughly proportional to the temperature rise

Table I

System	*Per cent reducing agent*	*Quantity measured*	*Number of measurements*	*Mean value of quantity*	*Root mean square deviation from mean*
$Fe/K_2Cr_2O_7$	45	V	5	5.5 *cm/sec*	0.4 *cm/sec*
	35	V	4	3.3 *cm/sec*	0.5 *cm/sec*
	55	T_2	9	1,038°C	50°C
$Mo/KMnO_4$	60	T_2	4	1,350°C	26°C
$Fe/KMnO_4$	80	T_2	3	840°C	5°C
Mo/BaO_2	40	T_2	3	1,630°C	20°C
	20	T_2	4	1,710°C	90°C
$Fe/KMnO_4$	50	$1/\Delta t$	3	1.58 sec^{-1}	0.29 sec^{-1}
	40	$1/\Delta t$	3	2.26 sec^{-1}	0.06 sec^{-1}
$Mo/KMnO_4$	70	$1/\Delta t$	4	2.88 sec^{-1}	0.80 sec^{-1}
Mo/BaO_2	10	$1/\Delta t$	4	0.094 sec^{-1}	0.009 sec^{-1}

The theoretical treatment given previously assumes that no heat is lost to the surroundings It was found that for pellets of $\frac{1}{2}$ in diam this condition was satisfied, because further increase in diameter did not increase V, and because the thermographs showed that the final temperature stayed sensibly constant for times large compared with Δt *Pace* Spice and Staveley, therefore, we believe heat loss in such pellets to be unimportant in our work

Table II Fe/BaO_2 (30 *per cent iron*)

Time sec / *Run*	−0.100	−0.050	−0.025	0	+0.025	+0.050	+0.100
1	4.90	3.85	3.14	2.20	1.25	0.80	0.35
2	4.95	3.25	2.60	2.00	1.50	1.15	0.25
3	4.00	3.95	3.50	2.05	0.70	0.40	0.10
4	3.90	4.25	2.70	2.00	1.40	0.75	0.10
Mean	4.04	3.57	3.00	2.06	1.21	0.77	0.17
Root mean square deviation	0.15	0.33	0.11	0.08	0.30	0.26	0.07

Propagation rates— These were determined as described by Spice and Staveley[1]

Ignition temperatures— Attempts to measure these were made in two ways *a* Pieces of compressed mixture were dropped into a hot tube, and the temperature at which half of them ignited was taken as the ignition temperature The results depended upon the size of the lumps, and some were anomalous in that ignition sometimes occurred for compositions in which the reaction would not normally propagate *b* The flat end of a compressed pellet, $\frac{1}{2}$ in diam, as used for propagation rate measurements, was brought smartly against the face of a heated steel block, and the lowest temperature required to ensure propagation was taken to be the ignition temperature This method did not give the second anomaly noted for the previous one

Thermal conductivities— These were measured, for iron barium peroxide mixtures only, with a double Lees disk apparatus[4], using special pellets 1.5 in diam and about 0.25 in thick The apparatus was calibrated with silica disks

Densities— These were obtained by measuring and weighing the pellets They are tabulated in *Tables IV* and *V* together with the proportion by volume of air to which they correspond

Analysis of slags— Both chemical and x-ray powder photograph methods were used to determine the nature of the reaction products

RESULTS AND DISCUSSION

The chemical nature of the burning reactions— If the burning reaction were a simple one, and if also the specific heats of reactants and products were equal and independent of temperature, the shape of the T_2/composition curve should be as in *Figure 2*, with a sharp peak at the stoichiometric point and a linear fall either side. Of the six systems investigated four show maxima and two do not (see *Figure 3* the slow sulphur/barium peroxide reaction is not comparable, because the range over which it can be investigated is too short) As would be expected, this behaviour is qualitatively the same[1] as that of the heats, q,

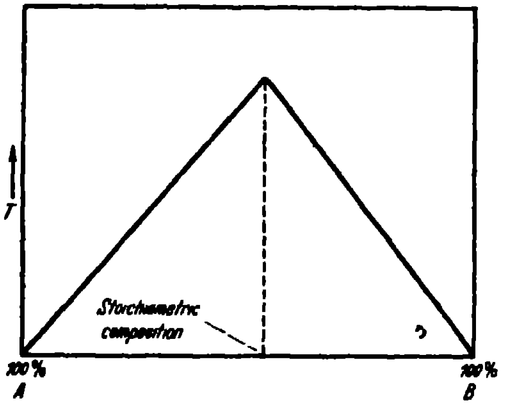

Figure 2

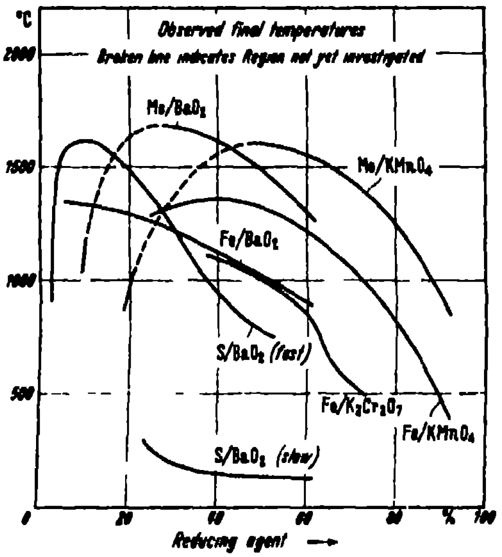

Figure 3

moreover, within the limits of experimental error, the four maxima in *Figure 3* occur at the same compositions as those in the heat curves

A better test for a simple reaction[1], is to see whether Q, the heat of reaction per mol of oxidizing agent, stays constant after a certain composition has been reached If it does, the reaction is simple and the point is the stoichiometric point if it does not, then probably a series of reactions is involved

Combining, so far as possible, such thermal evidence with the analytical evidence, the following conclusions are reached For molybdenum/barium peroxide and sulphur/barium peroxide (fast) the reactions probably are

$$X + 3BaO_2 \rightarrow 2BaO + BaXO_4$$

For iron/potassium permanganate and molybdenum/potassium permanganate systems, Q variations indicate stoichiometric points at 40 per cent and 50 per cent of reducing agent respectively the T_2 maximum agrees in the former case, but in the latter it probably is at a rather lower percentage

The absence of maxima in T_2 for the iron/barium peroxide and iron/potassium dichromate systems is hard to explain, because the most plausible reactions[1]

$$2Fe + 3BaO_2 \rightarrow FeO_3 + 4BaO \ .$$

and

$$7Fe + 3K_2Cr_2O_7 \rightarrow 3FeCr_2O_4 + 3K_2O + 2Fe_2O_3$$

give stoichiometric points at 19 per cent and 44 per cent iron respectively, which points are within the ranges investigated The x-ray analyses are compatible with these reactions but are inconclusive Q for the iron/barium peroxide system is, however, constant down to 15 per cent iron, thus indicating a different reaction

Test of the thermal conduction theory— Before applying the observed quantities V, k, d, c, T_0, T_1, dT/dt and $1/\Delta t$ to testing the Mallard-Le Chatelier theory, comments on some of them individually are necessary

The observed thermal conductivities of iron/barium peroxide pellets are given in *Table III* From their similarity and their smallness ($k = 0{\cdot}16$ c g s units for massive iron) they are evidently determined almost entirely by the conductivity of the air in the interstices*, though possibly the oxide films also reduce the conductivity We therefore use the same value for compressed pellets of any mixture with a metallic reducing agent For the sulphur/barium peroxide systems k is assumed to be 0 0016

Table III Thermal conductivities of iron barium peroxide mixtures

Per cent iron	$k \times 10^5$
0	159
20	154
40	165
60	171
80	174
100	184

Where specific heats of the components are available those of the compositions were calculated by the mixture law Spice and Staveley[1] assumed the molar heat for barium peroxide to be the same as that of the isomorphous substance calcium carbide, and thus obtained a value of ~0 1 for the specific heat Having regard for general experimental inaccuracies, we have, however, taken the values for all iron/barium peroxide mixtures to be that of iron, and those of sulphur/barium peroxide mixtures to be that of sulphur The values are tabulated in *Tables IV* and *V*

---

* For close-packing of uniform spheres the volume of air (*Table III*) is 26 0 per cent In fact, for low proportions of reducing agent the packing is usually better and for high ones worse than this The closer packing in the sulphur/barium peroxide system at high proportions of sulphur may be due to the relative softness of this component

The ignition temperatures measured with the hot block were found not to vary within a system save in so far that some mixtures would not ignite at all We therefore ascribe one value to each *viz*

Fe/BaO_2 600°C $Fe/K_2Cr_2O_7$ 400°C S/BaO_2(slow) 90°C

For the fast sulphur/barium peroxide reaction the value taken was T_s (slow) extrapolated to 25 per cent sulphur, at which composition the slow reaction would occasionally pass spontaneously into the fast one For the systems iron/potassium permanganate, molybdenum/potassium permanganate and molybdenum/barium peroxide the ignition temperatures were determined only by the furnace method The results are

S/BaO_2(fast)	250°C	$Fe/KMnO_4$	200°C
$Mo/KMnO_4$	200°C	Mo/BaO_2	300°C

It is unlikely that these values can be relied on to nearer than 50°, but fortunately they need not be known at all accurately

To test equation 3b, values of dT/dt at any temperature up to T_1 could be used The lower the temperature chosen, the more certain it would be that no reaction had occurred, but, because of the practical difficulties of reading slopes from thermographs, it was desirable to take them at the highest permissible temperature which was considered to be the observed ignition temperature

For the systems iron/potassium permanganate, molybdenum/potassium permanganate, and molybdenum/barium peroxide, the experimenter (R B T) considered that dT/dt could not be measured satisfactorily even at T_1, so results for these are used only to test equation 5b with dT/dt replaced by $(T_s - T_1)/\Delta t$ For the other systems, $(dT/dt)_{T_1}$ and $(T_s - T_1)/\Delta t$ are compared (*Table IV*), Δt, for ease of measurement being taken as $(\Delta t)^{T_s}_{T_1}$ Agreement is fairly good

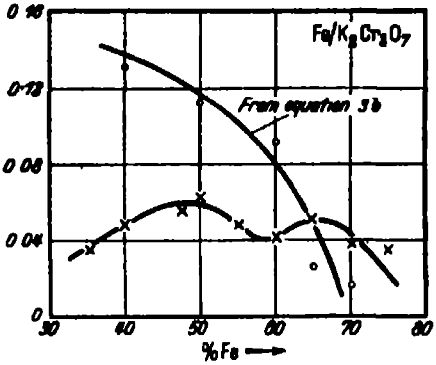

Figure 5

Table IV

Per cent reducing agent	Density	Vol of air (calc) per cent	Specific heat (calc)	$\frac{T_s - T_1}{\Delta t}$	$\left(\frac{dT}{dt}\right)_{T_1}$	$\left(\frac{dx}{dt}\right)_{ifx}$	$\frac{T_{ifx}}{T_s - T_1}$
			Iron/potassium dichromate				
40	2 76	25	0 16	2,100	1 550	1 88	0 60
50	2 94	28	0 15	1,800	1 200	1 90	0 59
60	3 23	28	0 15	650	900	1 00	0 54
65	—	—	—	73	75	0 14	0 38
70	3 57	29	0 14	41	24	0 06	0 37
			Iron/barium peroxide				
15	4 4	16	0 14	1 760	2 000	—	—
20	4 4	18	0 14	15,000	9 300	11 1	0 66
30	4 4	21	0 14	9,200	10,880	8 7	0 58
40	4 4	24	0 14	12,400	10 170	8 8	0 72
42 5	4 4	25	0 14	11,000	12,000	10 2	0 54
45	4 4	26	0 14	4 700	6,660	4 1	0 52
55	4 4	29	0 14	2 900	3,000	3 4	0 59
			Sulphur/barium peroxide (fast)				
2 5	4 05	16	0 18	2 270	2,900	3 2	0 49
5	3 93	15	0 18	12,200	8 500	8 0	0 56
10	3 77	13	0 18	12 200	3,520	10 0	0 56
20	3 40	10	0 18	2,300	4,300	3 8	0 41
30	3 09	10	0 18	1 900	1,710	1 5	0 34
40	2 81	10	0 18	600	1,040	1 2	0 48
50	2 57	10	0 18	580	720	1 0	0 56
			Sulphur/barium peroxide (slow)				
30	3 09	10	0 18	10 0	13 4	0 076	0 61
40	2 81	10	0 18	6 3	6 9	0 050	0 73
50	2 57	10	0 18	4 3	4 8	0 042	0 57

The first test of the theory is the comparison of observed and calculated values of *V*, the latter either from equation 3b or 5b [with $(\Delta t)^{T_s}_{T_1}$ as indicated on the figures (see *Figures 4* to *10*) The absolute rates are compared, and the relations within each system are shown by comparing $(V/V_{max})_{obsd}$ and $(V/V_{max})_{calc}$ In *Figures 4* to *10* × V_{obs} and $(V/V_{max})_{obsd}$ ○ V_{calc} ● $(V/V_{max})_{calc}$

For three systems (*Figures 4, 6, 7*) agreement for relative rates is good For three others (*Figures 8,*

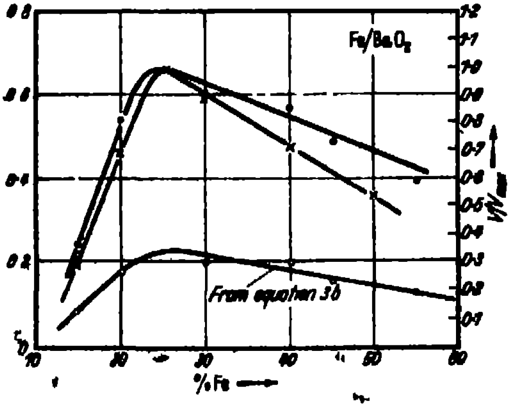

Figure 4

Table V

Per cent reducing agent	Density	Volume of air (calc) per cent	Specific heat (calc)	$\frac{T_2-T_1}{\Delta t}$ (mean)
		Iron/potassium permanganate		
25	2 76	15	0 19	790
30	2 85	15	0 19	2,600
40	3 05	17	0 19	3,100
50	3 16	21	0 18	2,410(interp)
60	3 45	23	0 18	2,090
70	3 61	28	0 17	1,280
80	3 77	31	0 17	650
90	4 21	36	0 16	96
		Molybdenum/potassium permanganate		
20	2 88	9	0 18	398
50	3 64	15	0 14	1 900
60	3 99	17	0 13	1 930
70	4 32	22	0 12	3 340
80	4 74	28	0 11	1,690
90	5 30	34	0 09	390
		Molybdenum/barium peroxide		
10	4 17	20	0 10	75
20	4 29	22	0 10	7 700
30	4 41	25	0 09	8,300
40	4 55	27	0 09	3,780
50	4 67	30	0 09	1 300
60	4 82	33	0 09	1,550

9, 10) it is fair, the observed maxima coming at somewhat higher percentages of reducing agent than the calculated ones Only for one (*Figure 5*) is it bad, this is the more surprising because measurements on this particular system are easiest

Absolute propagation rates agree well only for the slow sulphur/barium peroxide reaction In the iron potassium dichromate system the calculated values are on the whole too high, and in the other systems they are between three and six times too small

This discrepancy is probably systematic Of the various data used, thermal conductivities are the most suspect The actual width of the reaction zone is from 0 03 to 0 9 cm *i e* from two to sixty times the greatest particle diameter (0 015 cm) The treatment of the material as a continuum in considering heat conduction may not, therefore, always be justified

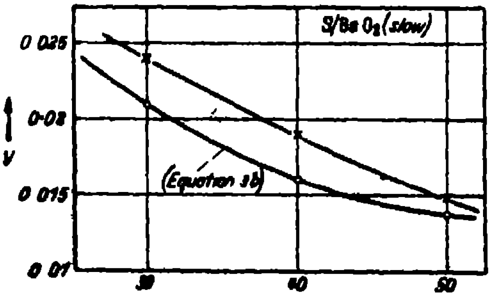

Figure 6

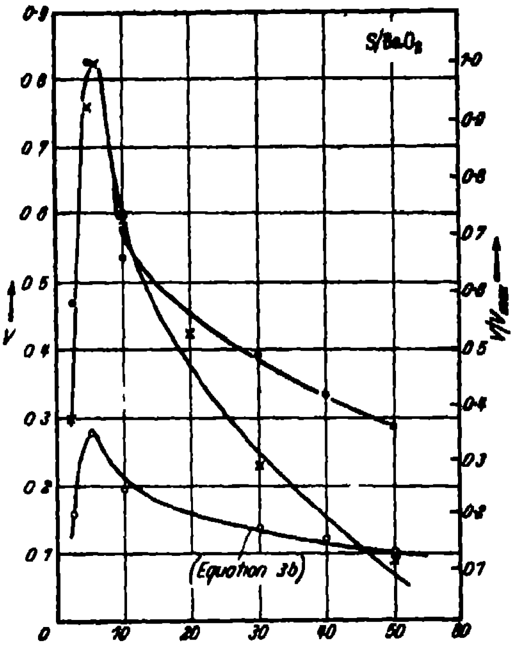

Figure 7

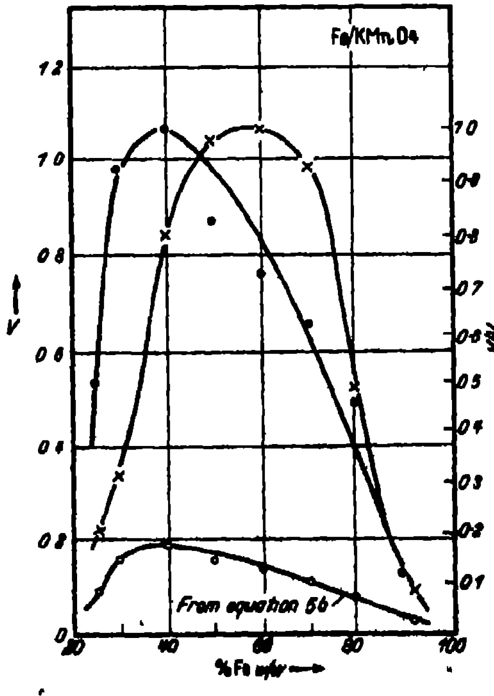

Figure 8

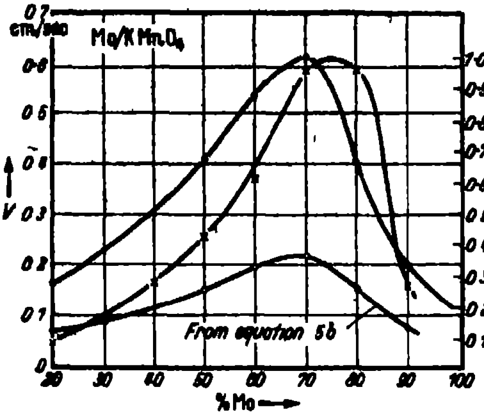

Figure 9

From an idealized representation of an equal binary system (*Figure 11*), it may be seen that, if the components have very different conductivities, the conductivity between *XX* and *YY* (parallel conductivity) will be much greater than that between *XX* and *ZZ* (series conductivity)

Parallel conductivity, effective over distances comparable with particle size, would rise steadily and rapidly with increase of metal content, whereas chance series conductivity, effective over long distances, would rise very slowly until a large proportion was reached and then would rise very rapidly, provided that metal to metal contacts were good, which from our measurements would appear not to be the case Therefore, if the former were the relevant quantity it would tend to cause an increase in *V* when other factors were tending to decrease it This may be the explanation of the major anomaly in the iron/potassium dichromate system in which otherwise there is no reason for expecting a maximum in *V* over the range of composition investigated It may also explain the lesser anomalies of the systems in *Figures 8, 9* and *10* where the maxima are displaced

We conclude that the theory that propagation of the reaction occurs only by thermal conduction is probably correct, though in its simple form it is hardly adequate The possibility of other propagation mechanisms must be borne in mind in particular, although the main products are not gaseous, hot gases are formed in the reaction zone and may be driven forward a short distance through the interstices, and so convey heat over and above that carried by conduction

Spice and Staveley's inference[1] that the maximum reaction rate occurs at a higher percentage of reducing agent than that for heat of reaction per gram, *q*, is

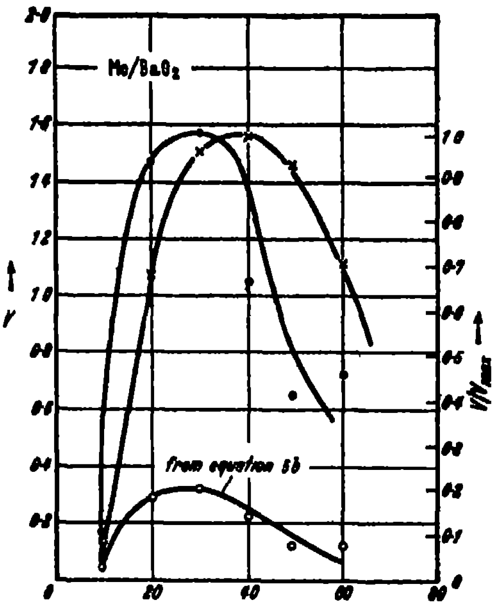

Figure 10

supported by some of our results Their further hypothesis, that this accounts for the relative positions of the maxima in *q* and in *V*, is not corroborated This may be seen by comparing the compositions at the maxima in *q*, in $1/\Delta t$ which is a rough measure of overall reaction rate, and in two or three systems in which all three quantities have maxima

Table VI

System	*w* (wt per cent composition for maximum)		
	q	$1/\Delta t$	*V*
Fe/KMnO₄	38	55	65
Mo/KMnO₄	52	70	75
Mo/BaO₂	19	25	38

By the first inference *w′* should be greater for $1/\Delta t$ than for *q* this is so, especially for Mo/KMnO₄ where strongly protective molybdate coatings may be formed The second one implies that the maxima in $1/\Delta t$ should come at a greater value of *w′* than those in *V*, which they do not In our view the differences in *w′* values for $1/\Delta t$ and for *V* may

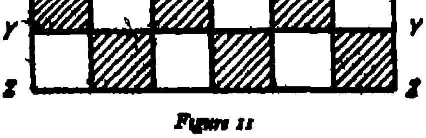

Figure 11

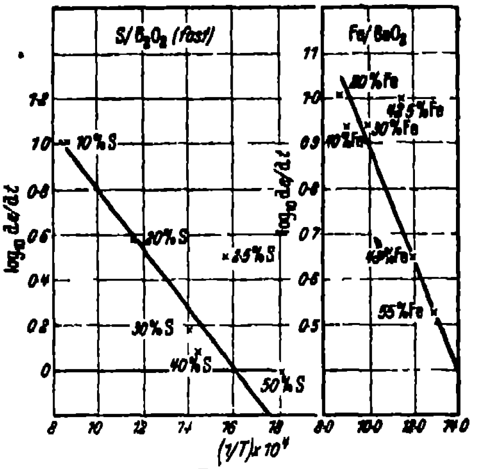

Figure 12

possibly be a consequence of parallel conductivity, and not chance series conductivity, being effective

Rates of reaction from thermographs— In *Table IV* are tabulated values of $\frac{1}{T_1 - T_0}\left(\frac{dT}{dt}\right)_{T_{if_x}}$ which, by equation 6, give $d\epsilon/dt$ These rates of reaction are obtained at different temperatures, but at roughly the same stage of reaction because the ratio $T_{if_x}/(T_1 - T_0)$, which is also tabulated and which may be regarded as a measure of ϵ at T_{if_x}, varies only over a range of about 0 2 in each system The wide variations from system to system and within some systems are noteworthy

We expect the rate to be given by an expression of the form

$$\frac{d\epsilon}{dt} = B(1 - \epsilon)^n \exp(-A/RT)$$

(*cf* p 002) in which n, the reaction order, probably is between 0 and 1 Since ϵ is much the same at all the inflection points in a given system (see *Table IV*), a plot of $\ln (d\epsilon/dt)$ against $1/T_{if_x}$ should give the activation energy A *Figures 12* and *13* show that nearly all the points fall on straight lines These results indicate that one reaction predominates in each system, which conclusion is, on the whole, supported by other evidence (*cf* p 004) It might be supposed that marked anomalies indicate the onset of other reactions, but this appears not to be so In the fast sulphur/barium peroxide reaction, for example, analysis shows that with 2 5 per cent sulphur the reaction is the same as that at the stoichiometric point, but at 50 per cent sulphur it is very different, yielding sulphides and sulphur dioxide nevertheless, the point for 50 per cent sulphur is nearer the mean line than that for 2 5 per cent

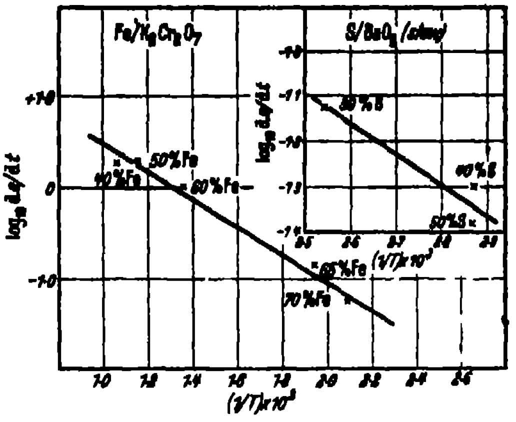

Figure 13

Table VII

System	T_1 K	A (cals)
Fe/K$_2$Cr$_2$O$_7$	673	6 900
Fe/BaO$_2$	879	5 700
S/BaO$_2$ (*slow*)	363	3 100
S/BaO$_2$ (*fast*)	593	7 850

The activation energies are given in *Table VII* and are compared with the ignition temperature in °K there is little correlation They are comparatively low, being 3 to 8 kcal/mol, and probably are much smaller than those for the pre-ignition reactions[1], which from the published results appear to be at least 50 kcal It is probable, therefore, that the rate-controlling processes for the reactions which lead up to the ignition are quite different from those which follow when the reaction is fairly started, as if something like a phase change has first to be brought about

The authors wish to thank Professor Sir Cyril Hinshelwood, F R S, Dr E J Bowen, F R S, and Mr L A K Staveley for helpful discussions while the experimental work was in progress, also Mr J S Dick, M B E, Senior Principal Scientific Officer of the Ministry of Supply, and his colleagues for their invaluable advice and help, and to the Chief Scientist, Ministry of Supply, for permission to publish this work

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Research Correspondence

Determination of Natural Sources of Vitamins D

IT is a well established fact that vitamins originate from green plants and are supplied from there to all living creatures. However, there is some doubt about the vegetable origin of the anti-ricket vitamins, vitamins D. Most investigators have not succeeded in detecting reasonable amounts of vitamins D either in green plants or in green sea algae, and since these vitamins are not thought to be produced by the lower animals their origin has never been satisfactorily explained. An exception is found in new-mown hay considerably exposed to the sun, which shows the formation of some vitamin D. In textbooks and reviews the source of vitamins D is considered a mystery[1]. The author has published papers on vitamins D in green plants[2-4] and has described their occurrence and the methods used for their detection. The reason why these vitamins are not usually found by other investigators has not been made clear in these papers and will be briefly discussed.

The amounts of vitamins D present in green plants are not very high. If direct feeding investigations are made, considerable amounts of vegetables must be given to experimental animals, and these vegetables also contain mineral matter. The diets are then most unnatural. For the experimental production of rickets the phosphorus content is determined and a large amount of calcium in the form of calcium carbonate is added to bring the calcium/phosphorus ratio to 4. Often the amount of calcium is added without analysis. When greater amounts of other materials are given the quantities of basic diet consumed are reduced in the same proportion and the quantities of phosphorus available are reduced accordingly. The amount of calcium is already high, and this may be increased by calcium from the minerals in the plants under investigation. The latter also contain other minerals which disturb the balance of the diet and according to the author mask the effect of the vitamins present[5].

To obtain trustworthy analyses of vitamins D in green plants a different procedure must be adopted. The vitamins D contents may be easily determined by use of the ether extract of vegetable products; this has no mineral content and a concentrated vitamin content. Vitamins D are fat-soluble and relatively stable. The ether extracts are obtained by extracting the dried and finely powdered materials with ether in a Soxleth apparatus under carbon dioxide. These extracts usually amount to from 4 to 5 per cent of the dry material. The amounts of vitamins D are easily determined, the dosage being accurate and reliable.

The author has tested the vitamin content of a series of plants in this manner. The contents in the ether extracts vary from 50 to 400 i.u. of vitamin D per gram; the corresponding contents in the dried materials are thus 2.5 to 20 i.u. vitamin D per gram. This corresponds more with the vitamin content of natural butter, about 1 i.u. per gram, than does the assumption that green plants are vitamin D free.

The author has similarly determined the vitamin D content of drifting green sea algae collected in a landing net and has found still higher values than in the land plants. The large vitamin D content of cod's liver is therefore no mystery.

The D vitamins found in green plants differ slightly in chemical composition and properties. Normally all the vitamin D content of oils is found in the unsaponifiable fraction, but only about one quarter of the vitamin D of plants is found there; the remaining three quarters is found in the saponifiable fraction. Hence the determination of D vitamins in green plants is restricted to biological tests.

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Note on the Emission of Positive Ions from Heated Glasses

HEATED salts on metal strips have long been used as sources of alkali positive ions[1], and in particular MURAWKIN[2] has used powdered glasses as efficient ion sources. The mechanism of the ion emission has always been somewhat obscure, although experiments have shown, using oxide mixtures, that the emission may be regarded as a thermal ionization process at the surface, due to the high work function of the mixture, in the manner suggested by LANGMUIR[3]. This explanation demands that the source mixture be capable of conducting electronically to the base metal used as a heating strip. In the case of glasses it is now accepted that they conduct electrolytically, the current being carried by alkali ions[4]. On this basis the following experiments seem to show that heated glasses can emit positive ions thermionically.

In all the experiments long glass tubes (or rods) were used as specimens. These were always made insulating by heating before use. The free ends of the specimens were heated over a small circular area to a whitish yellow heat by means of an oxy-coal gas flame This method of heating did not allow any quantitative results, but as large specimens were used and the presence of nearby conductors particularly avoided this was the only simple means of heating An ordinary gold leaf electroscope charged to 600 volts was used throughout as a current detector

It was first shown that only soda glass specimens would tend to discharge the charged electroscope when removed from the flame and held over the electroscope cap. When an earthed conducting wire was inserted in the specimen tube so that it made contact with the glass surface near the heated end, it was shown that both soda and pyrex glasses gave complete discharges of the electroscope when this was negatively charged When the electroscope was positively charged soda glass gave a small discharge effect, while pyrex had no effect An explanation of these effects is that heated pyrex and soda glasses give rise to a positive ion emission which will discharge an electroscope negatively charged, provided that an earthed wire forms part of the discharge circuit Soda glass must also give rise to a negative ion emission of small dimensions which does not demand a complete circuit for detection As it is most unlikely that glasses would give rise to a negative ion emission, it is suggested that thermal ionization of alkali vapour occurs above heated soda glass but not pyrex The presence of alkali vapour above heated soda glass is easily detected by using moistened red litmus paper, but less readily above pyrex

The above explanation was supported by other experiments in which the contact wire inside the glass tube was connected to a 600 volt dry battery instead of directly to earth The opposite pole of the battery was connected to the detecting electroscope case Specimens were again heated and then held over the electroscope, which was uncharged It was found that, with the contact wire positive, the electroscope was fully charged by the emission from both types of glass The charge on the leaf was easily shown to be positive. When the contact wire was negative, only soda glass charged the electroscope slightly

It is deduced that positive ion emission only takes place from heated pyrex glass in bulk form when a complete charging or discharging circuit is provided By moving the wire in the above experiments it is demonstrated that this circuit is completed in the glass only when contact is made with the conducting part of the tube near the heated end Since glass is only a good conductor at elevated temperatures, it suggests that any charging or discharging current utilizes the normal ion carriers in the glass. Hence it would seem that the emitted ions are the actual current carriers from the glass.

In the case of soda glass it appears that some positive ion emission is due to volume thermal ionization of alkali vapour which also gives negative ions There is no doubt that this process would take place with pyrex glass at more elevated temperatures

Although the above discussion has been confined to glass ion emitters where the conducting process in the bulk of the substance is known, it is possible that a similar process occurs in other types of positive ion emitters The fact that soda and pyrex glasses show such distinctive behaviour when a negatively charged wire is inserted in the heated glass may be used as a practical test for distinguishing between the two types of glass

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Crystal Structure of Acridine III

Acridine, $C_{13}H_9N$, crystallizes in at least three distinct forms[1], only one of which is reported by Groth[2] The structure of one of these, provisionally called acridine III, has now been determined

Crystals of acridine III are obtained from solution in dilute alcohol They are prisms, elongated along [010] and bounded by the {101} and {101} faces. {100} is developed occasionally X-ray photographs show that the Laue symmetry is $2/m$ and hence that the crystal system is monoclinic The unit cell dimensions, obtained from measurements of oscillation and rotation photographs and accurate to about 1 per cent, are, Å, $a = 11\ 5$, $b = 6\ 03$, $c = 13\ 7$; $\beta = 99° \pm 1°$ The density, measured by flotation in potassium bromide solution, is 1 265 gm cm^{-3}, and the number of molecules in the unit cell is 4. Reflections $h0l$ are absent when $(h + l)$ is odd, and reflections $0k0$ are absent when k is odd. There are no other systematic absences so that the space group is uniquely determined as $P2_1/n$

Reflections $h0l$ were recorded on multiple-film Weissenberg photographs, using copper radiation, and the intensities were estimated visually Examination of these intensities led to the conclusion that the structure possesses the following characteristics *1* densely populated (201), (20$\bar{2}$), (70$\bar{3}$) and (3,0,$\overline{11}$) planes, *2* an approximate quartering in the [101] direction. Structure factors were calculated for a

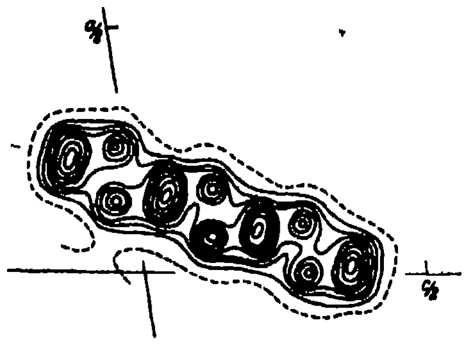

Figure 1 Electron density in one acridine molecule projected on (010) *The contours are at intervals of one electron per* Å², *the one-electron line being broken*

trial structure based on these features, they agreed well with those observed, and the normal processes of Fourier refinement have given the map of electron density projected on (010) shown in *Figure 1* The reliability index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, for this zone of reflections is now 0 20

It is not yet possible to make any definite statements about the detailed structure of the molecule, there are as yet no significant indications that it is other than planar Investigations of this point, and determination of the bond lengths for comparison with those predicted by the theory of molecular orbitals[3], are the objects of further work

It is apparent from the projection of the molecule and from packing considerations that the intermolecular distances are very similar to those reported in anthracene[4] The arrangement of molecules in the unit cell viewed along [010] is shown in *Figure 2*.

My thanks are due to Dr A J C Wilson for his guidance and for the use of apparatus purchased with a Royal Society grant I am indebted to the University of Wales and the Department of Scientific and Industrial Research for financial assistance

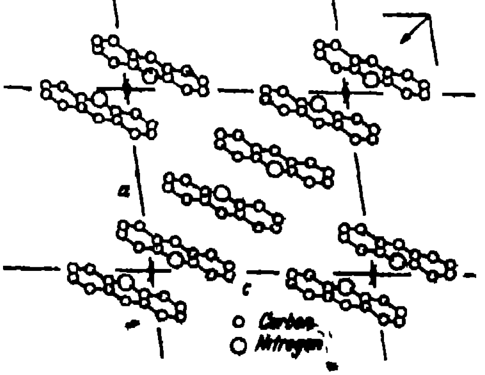

Figure 2. Arrangement of molecules in the unit cell

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The Blue Sun

Over a large part of the country on the afternoon and early evening of 26 September 1950 the sun appeared as a vivid blue disk Most of the explanations put forward do not seem to be in accordance with accepted physical principles *e g* scattering of light by a smoke cloud from forest fires in N America

The essential points which have to be explained seem to be as follows *1* blue light was transmitted through the atmosphere *2* light of any other colour was not so transmitted These can be explained most simply by dispersion, not by scattering, and it is suggested that the atmospheric conditions were such as to reproduce the effect of a Christiansen filter[1]. This consisted of glass particles suspended in a mixture of benzol and carbon bisulphide For light of one wavelength the refractive index is the same for glass and liquid, therefore this light passes through undeviated However, owing to the difference in dispersion the refractive indices for other wavelengths are different and therefore light of these wavelengths will be deviated and dispersed Liquid emulsions provide a more flexible system and a convenient one for demonstrating the effect is formed as follows[2] Shake up equal volumes (the ratio is not important) of glycerin and acetone The acetone should contain about 4 per cent collodion to stabilize the emulsion. To the milky emulsion, which consists of glycerin globules floating in acetone, benzene is added slowly The milky appearance will disappear and the emulsion will become clear and transparent If a white light is viewed through such an emulsion in a parallel sided glass vessel the light will appear coloured and by adding either benzene or acetone the colour will change from wine-red through green to violet-blue. The optical properties of such ‘chromatic emulsions’ have been examined experimentally and theoretically by Sogani[3] The effect is very striking and provides an excellent demonstration, reproducing exactly the effect of the ‘blue sun’.

It seems that this is the most probable explanation of the phenomenon and that by some curious, and rare, meteorological conditions there was a layer at about 30,000–40,000 ft consisting of two media, maybe two gases, taken up and kept separate in some way Airmen who flew high enough to observe the sun in its natural colour report that they passed through a 'brown haze' between 30,000 and 40,000 ft[4] It is significant that one of the above emulsions which transmitted blue light appears to be amber when viewed at right angles to the beam

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Relation between Structure and Melting Point in Aromatic Compounds

Two attempts have been made in recent years to correlate the structure of aromatic compounds with their melting points Chatt and Wynne[1] examined the melting points of ten series of naphthalene compounds of the type $C_{10}H_6R_2$ (ninety two of the possible hundred compounds being quoted) Dividing the compounds according to their two dimensional symmetry three groups were obtained —*A* compounds without symmetry 1,2 , 1,3 , 1,6 , and 1,7 isomers, *B* compounds with a plane of symmetry 1,4 , 1,8 , 2,3 , and 2,7 isomers, *C* centro-symmetrical compounds 1,5 , 2,6 isomers With nine exceptions (contained in six different groups) the compounds in group *B* had higher melting points than those in group *A* Furthermore with one exception the 2,6 isomer in group *C* had the highest m pt of all , the remaining 1,5 isomer always had a m pt higher than those in group *A* but some were lower than corresponding ones in group *B* These authors argued therefore that such a relationship might also apply to the tetrasubstituted naphthalenes (there being insufficient data to examine these) and used this as supporting evidence for their orientation of 1,3,5,7-tetranitronaphthalene Hodgson and Ward[2] commented upon this and pointed out that the available data for the tetrachloronaphthalenes were not in complete agreement.

Holler[3] (who incidentally made no reference to the above work) later examined the melting points of ninety seven series of disubstituted benzenes and postulated the following rules For compounds containing one *meta* orientating group and one *ortho-para* orientating group the order of melting points is $p > m > o$ whereas for compounds containing only *meta* or only *ortho-para* orientating groups the order of melting points is $p > o > m$ The first class contained forty one series of compounds and there were twelve exceptions , there were fifty six series in the second class with eighteen exceptions No explanation was advanced for these results , as with Chatt and Wynne's work the theories were purely empirical

We have now re-examined the data of Holler on the same basis adopted by Chatt and Wynne, namely two dimensional geometrical symmetry *Para* compounds always have a higher degree of symmetry than corresponding *ortho* or *meta* ones, being centrosymmetrical for identical substituents and having a plane of symmetry for different substituents *Ortho* and *meta* compounds only have a plane of symmetry for identical substituents, otherwise being unsymmetrical Significantly it was found that in ninety two of the ninety seven series the *para* compound had the highest *m* pt It may also be noted that there were twenty eight exceptions to the expected order for *meta* and *ortho* compounds in the data cited by Holler It appeared to us therefore that a simple division of the disubstituted benzene derivatives into *para* and *ortho-meta* compounds on this geometrical basis was a much more satisfactory division than that suggested by Holler It then can be said that the order of melting points is $p > o,m$

We thought that it would be useful to apply these concepts to other aromatic nuclei but amongst the mononuclear compounds could only find appreciable data for the monosubstituted pyridines For seven series of compounds the γ-isomer, which has a plane of symmetry, had the highest m pt in six cases, the order for these six cases being $\gamma > \beta > \alpha$

We have extended Chatt and Wynne's examination of the disubstituted naphthalenes to compounds containing similar and different groups We have considered forty five series of compounds, about five hundred compounds in all We were unable to formulate any rules similar to those advanced by Holler (considering such facts as 'quinonoid' and 'non-quinonoid' positions[4]) The only significant results that we observed were that *a* for fourteen complete series of isomers the 2,6 isomer had the highest m pt ten times, and was second highest twice , *b* for forty series of isomers where the m pt of the 2,6 isomer is known this m. pt was highest nineteen times and second highest six times , *c* for the fourteen complete series a quinonoid compound was highest or second highest twenty two times from the possible twenty eight , *d* for the forty five series a 'quinonoid' compound had the highest m pt thirty eight times

We are extending our observations and hope to publish complete results at a later date

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Penicillin Production With Lucerne

NUTRITIONAL requirements have been found to influence the yield of metabolic products of micro-organisms in general The studies of the author on bacterial amylase production have shown that different substrates such as castor-seed cake, wheat bran, lucerne *etc* influence the amylase activity of *B subtilis* to a considerable extent During these studies wheat bran and lucerne have been found to constitute excellent substrates[1] Wheat bran has been employed successfully as a substrate for obtaining high yields of penicillin[2] As lucerne was found to vie with wheat bran in the bacterial amylase production the question arose whether lucerne could serve equally well as a substrate for penicillin formation by *Penicillium notatum* The present investigations are therefore concerned with the study of lucerne as substrate for penicillin production, using *P notatum* (N R R L 832) obtained from Northern Regional Laboratories

The production of penicillin on lucerne was studied while employing different ratios of lucerne powder to phosphate buffer solution (Sørensen's) in order to find the optimum moisture needed for the fungus to synthesize penicillin The experimental procedure for obtaining the results was as follows

10 gm of lucerne powder was taken in a 250 ml conical flask and moistened with a known volume of phosphate buffer solution (*p*H 7 0) to give the required ratio between substrate and diluent The culture medium was sterilized at a pressure of 15 lb/in^2, for 30 min and then inoculated with the fungal spores Incubation was carried out at 28°C for 3 days The penicillin formed was then extracted with 25 ml of water at room temperature The mould was strained through cheese cloth and the extracts thus obtained were analysed for their antibiotic activities For comparison, wheat bran medium was employed during these investigations The antibiotic activity was determined by the 'cup assay' method[3] The results are given in *Table I*

Table I Influence of ratio of substrate to diluent on the penicillin production

Ratio of substrate to diluent	*Results expressed as diameters of the cleared zones (mm)*	
	Wheat bran	*Lucerne*
1 1	11 5	0 0
1 1 5	23 0	0 0
1 2	21 0	11 0
1 2 5	18 5	21 0
1 3	—	24 0
1 3 5	—	16 0
1 4	—	15 0
1 5	—	13 0

The results presented in *Table I* clearly indicate that lucerne when moistened with phosphate buffer in the ratio of 1 3 yields as much activity as one could secure with wheat bran These investigations were further carried out to determine the effect of the period of incubation on the formation of penicillin Throughout these experiments the ratio of lucerne to phosphate buffer employed was 1 3 The antibiotic activity was determined after every 24 hours of incubation period The results are given in *Table II*

Table II Effect of incubation period on penicillin formation

Incubation period (days)	*Antibiotic activity diameter of the cleared zones (mm)*	*p*H *of the extracts*
1		—
2	21 0	7 1–7 2
3	24 0	7 1–7 2
4	19 5	7 1–7 2
5	13 0	7 1–7 2
6	12 0	7 1–7 2
7	10 5	7 1–7 2

The experimental data presented in *Table II* have shown that antibiotic activity is maximum after the third day of the growth of the fungus The *p*H of the medium during growth is constant throughout

The results obtained with lucerne as the substrate for the growth of *Penicillium notatum* further indicate that lucerne could effectively replace wheat bran in the production of penicillin Based on these data, crude penicillin powder was produced on a semi-large scale with lucerne as the substrate, using a series of 4 litre wide bottomed culture flasks.

The above findings are also in conformity with the results obtained with the highly amylolytic strain of *B subtilis*, where lucerne has given similar favourable results in the formation of bacterial amylase. The foregoing results appear to indicate that lucerne may form as good a nutritive material as wheat bran for the growth of micro-organisms in general Further work is under progress to study the growth of the *Penicillium notatum* in a liquid medium employing various extracts of lucerne powder

Sincere thanks are due to Professor V Subrahmanyan and Colonel S S Bhatnagar for their keen interest

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The Chemical Silvering of Non-metallic Surfaces

THE recent work reported by UPTON and HERINGTON[1] on this subject is closely related to an investigation undertaken in this laboratory A general theory has been developed covering the processes occurring in such systems

The reaction occurring in silvering solutions may be divided into three stages *1* reduction $Ag^+ + e \rightarrow Ag$, *2* formation of a silver sol, *3* flocculation of the sol and precipitation of metallic silver The mechanism of *1* depends on the reducing agent In general the reaction occurs more rapidly on surfaces than in solution, and is thus autocatalytic unless the surfaces of the colloidal silver particles are blocked by adsorption of an 'inhibitor'

The stability of the sol *2* will be a function of the proportion of stabilizing agents (protective colloids or strongly adsorbed negative ions), and flocculating agents (electrolytes and strongly adsorbed positive ions) present in the solution. The location of the metallic silver eventually deposited depends on the relative flocculating power of the surfaces and that of the solution If these ideas are correct efficient silvering will involve such control of the initial reaction that silver is produced more slowly than the ultimate deposition rate on the desired surface In addition a stable reservoir of colloidal silver should accumulate and flocculation should occur only on the active surfaces The author has developed such a process[2] A specific example illustrates the fundamental principles I C I surface active agents have been used in this investigation as examples of the various classes *Lissapol N*, non-ionic *Lissapol C*, anionic *Fixanol C*, cationic

Perspex specimens were well cleaned with *Teepol* and water, soaked for 10 minutes in an aqueous activating solution of stannous chloride 5 per cent; hydrochloric acid 5 per cent, *Lissapol N* 0 005 per cent, rinsed in running water for 5 minutes, and immersed in the silvering solution, made by adding to a 1 per cent silver nitrate solution *Lissapol C* and a known excess of ammonia Prior to silvering 0 2 cc of a 4 per cent solution of formaldehyde was added

In solutions containing no excess ammonia the rate of reduction of the silver ions and formation of a silver sol decreased as the concentration of *Lissapol C* was increased from zero to 0·2 per cent The induction period, before metallic silver appeared, increased from a few seconds for these solutions containing no surface active agent, to many hours for the higher *Lissapol C* concentration The ratio of silver deposited on the unactivated glass walls of the container to silver deposited on the prepared surface decreased as the amount of *Lissapol C* increased Increasing the amount of ammonia increased the time scale of the whole process

Cationic surface active agents, for example *Fixanol C* in concentrations below 0 002 per cent, in the absence of excess ammonia, showed an effect similar to that of *Lissapol C*, although adhesion of the deposited silver was less good, above this concentration, however, the presence of *Fixanol C* caused a rapid precipitation of a silver sludge In the presence of a large excess of ammonia, pyridine *etc* (1–10 per cent ammonia) it was possible to reduce this flocculating effect of the *Fixanol C*

Complexing agents in excess reduce the free silver ion concentration and hence the rate of the reduction *1* above Many surface active agents inhibit this reaction With the two discussed above, this inhibitive effect reaches a maximum at concentrations of less than 0 01 per cent

The contrasting behaviour of the two types of surface active agent in greater concentrations results from their effect on the silver sol The active anionic component of *Lissapol C* carrying a charge of the same sign as the silver colloid particle will increase the stability of the colloid when it is adsorbed, the active cationic component of the *Fixanol C* will neutralize the colloidal charge and produce flocculation

The activating property of stannous chloride solution depends on the presence of positively charged colloidal stannic hydroxide, which is adsorbed on the surface during activation When such a prepared surface is silvered the negatively charged silver particles are discharged and precipitated preferentially on this film of stannic hydroxide The *Lissapol N* stabilizes the colloidal stannic hydroxide. The simple adsorption of stannous ions may play an important part, particularly in freshly prepared activating solution. The behaviour of *Fixanol C* described by Upton and Herington thus appears to depend on the presence of a considerable excess of a complexing agent that reduces the silver ion concentration, and *b* a quantity of *Fixanol C* sufficient to inhibit the initial reduction without coagulating the colloidal silver

The process developed by the author requires no large excess of complexing agent, is not critically dependent on the amount of surface active agent, and using the activating solution described is extremely effective for silvering surfaces that possess groups of sufficient polarity to adsorb a film of stannic hydroxide Polystyrene surfaces have proved difficult to silver, and polythene and polytetrafluorethylene impossible

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The Solubility of Colchicine in Water

ACCORDING to the *British Pharmacopœia* colchicine is readily soluble in water[1] The *U S Pharmacopeia* specifies a solubility of 1 part in 22 parts of water[2], and, in a later edition, 1 in 25 parts of water[3] In each case cold water is presumably to be understood On the other hand it can readily be shown that pure crystalline colchicine dissolves completely in only 3 parts of cold water, and that the solution on standing deposits a sesquihydrate, of which the solubility is not more than 1 in about 70 parts of water (These last two observations were first made by MERCK[4], who was however using an amorphous material) Furthermore, on warming strong aqueous solutions of colchicine, a turbidity is produced which vanishes on cooling, presumably because colchicine is less soluble in hot water than in cold This complex behaviour appears to have been generally overlooked

The matter came to our notice in course of examining a commercial sample of crystalline colchicine which had been adjudged unsatisfactory, on *U S Pharmacopeia* standards, because of its low solubility in water The sample was found to consist essentially of high quality colchicine, but it dissolved incompletely in 25 parts of cold water, and the solution, whether untreated or filtered by suction, slowly deposited large crystals of colchicine sesquihydrate (Found C, 61·5 per cent, H, 6·55 per cent in an air dried specimen, or C, 61 4 per cent, H, 6 6 per cent after heating 1 hr/100°/18 mm. Calc for $2C_{22}H_{25}O_6N \cdot 3H_2O$. C, 62 0 per cent, H, 6 6 per cent). At the same concentration the clear solutions which were obtained from pure anhydrous colchicine[4] could be preserved for several days, but they also deposited the hydrate within a few hours of being seeded with it Moreover, independently of source, these hydrate crops, when dissolved in their mother liquors by gentle warming—necessarily prolonged to procure complete dissolution—afforded lasting solutions, which again crystallized on being seeded Although the precise solubility of the hydrate was not determined, Merck's estimate is confirmed by the observation that a speck of the powdered substance grew into a small but well defined crystal when immersed in a solution of colchicine in 60 parts of water As already indicated the hydrate crystallizes, apparently spontaneously, from highly concentrated solutions of colchicine in water

Colchicine sesquihydrate, after sintering at 135–140°C with presumed dehydration, melts at 148–151°C, and this melting point is unaffected by admixture of anhydrous colchicine (m pt 154–155°C) The two compounds cannot therefore be distinguished satisfactorily by melting point The x-ray diffraction powder photograph, however, constitutes a virtually absolute 'finger print' of a given crystalline species, and the diagram I obtained with anhydrous colchicine proved to be quite distinct from that II with specimens of the hydrate Finally a photograph was taken of the small, sparingly soluble residue left when the commercial sample of colchicine was shaken for 5 min with 25 parts of water This diagram was identical with II, thus proving the residue to be colchicine sesquihydrate

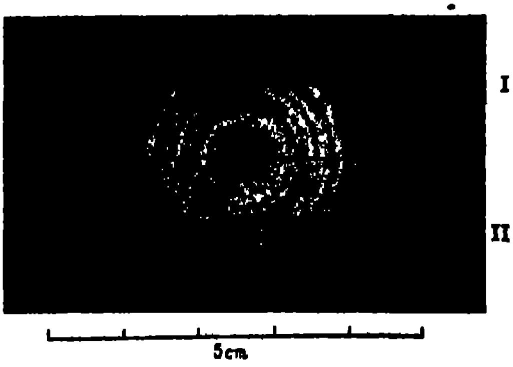

Figure 1 Powder photograph of colchicine (I) and its sesquihydrate (II), taken with Cu Kα radiation in a camera of radius 3·0 cm

These observations suggest that the system colchicine/water resembles sodium sulphate/water[5]. In both there exist near room temperature a hydrate of lower, and a metastable anhydrous form of higher, solubility, the former solubility rising, and the latter diminishing, with rise of temperature The negative temperature coefficient of the anhydrous colchicine indicates that dissolution is exothermic, which might be expected if the process is accompanied by chemical change

The important fact is that in presence of water anhydrous colchicine is metastable and cannot exist in true equilibrium with aqueous solutions The sesquihydrate appears to be the stable form Accordingly the solubility requirement of 1 part in 25 parts of cold water can be met only by chance—the chance that the sesquihydrate is not formed On the basis of general experience this chance appears to be a good one, at least over a period of some days it becomes negligible when pre-formed solid hydrate is present

We thank Professor J W Cook, F R S, for his interest in this investigation

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Mixed Adsorption of Hydrogen and Carbon Monoxide of Fischer-Tropsch Catalysts

In a previous communication[1] the authors reported that on a Fischer-Tropsch catalyst (A) containing 34 per cent Co, 4 per cent Cu, 2 33 per cent ThO$_2$, 0 24 per cent Ce$_2$O$_3$ and the rest kieselguhr, the adsorption of hydrogen from 1 CO 1 H$_2$ and 1 CO 2 H$_2$ mixtures, at temperatures between 25° and 97°C and mixed pressures below 76 cm, was greater than from pure gas at equivalent pressures At the same time there was a suppression of carbon monoxide adsorption from the mixtures Under these conditions no trace of hydrocarbons was found in the adsorption system

These investigations have since been extended to another cobalt catalyst (B) which contained 4 per cent Cr$_2$O$_3$ in addition to the ingredients of catalyst A This addition of chromium oxide was found by Ghosh and Basak[2] markedly to improve the yield of benzine and also to facilitate the use of watergas (1 CO : 1 H$_2$) without the usual enrichment of H. When the adsorptions of pure carbon monoxide and hydrogen by catalyst B were compared with those from their mixtures at equivalent partial pressures it was found that, in contrast with our experience with catalyst A, the adsorption of carbon monoxide was enhanced at all the temperatures studied (25°–97°C) while that of hydrogen suffered suppression at temperatures up to 76°, but was enhanced at higher temperatures The adsorption of carbon monoxide at higher partial pressures was found to be greater from the 1 CO 2 H$_2$ than from the 1 1 mixture, while the reverse was true of hydrogen adsorption That is, the adsorption of either gas was greater from that mixture in which its concentration was lower

On both catalysts it has been observed that the adsorption of each constituent commenced to crease with temperature at much lower temperatu in the presence of the other gas than in the absen of the latter These facts point to the possibi progressive formation of a CO-H complex o surface of the catalyst If the simultaneous a tions of the constituent gases were plotted a each other the 'isotherms' so obtained te become linear at the higher temperatures, [illegible] every 2 cc increase in CO-adsorption that of gen increased by nearly 1 cc This aga CO-H complex formation It therefore a the chemisorbed CO-H complex, rather t he cobalt carbide, may be the intermediate in er-Tropsch synthesis by catalyst B

The employment of a built-in thermal uctivity meter facilitated continuous observation of the progress of mixture-adsorption After [illegible] first five minutes the adsorption of hydrogen dec[illegible]sed while that of carbon monoxide increased portion until, eventually, a state of saturation was reached with respect to either gas Thus a p[illegible]l replacement of adsorbed hydrogen by ca[illegible] monoxide took place during the synthesis of C[illegible] H complexes on the catalyst surface

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